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MODERN COKING PRACTICE

BY

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WIGAN COAL AND IRON CO.

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INCLUDING THE

Analysis of Materials and Products

BY

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Volume II

BY-PRODUCTS

With numerous Illustrations



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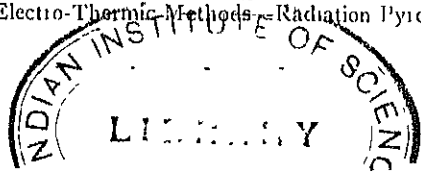
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MODERN COKING PRACTICE

CHAPTER I

INTRODUCTORY

IN modern coking practice coal is subjected to closed distillation, and in the oven a primary separation of volatile matter and solid residue takes place. The first volume has dealt with the solid residue, and the object of this second volume is to describe the modern method of extracting from the volatile matter the valuable constituents, tar, ammonia, and benzol, generally known, collectively, as by-products.

Though not usually classed as a by-product, the surplus gas from a coke plant is of considerable importance, and a consideration thereof is accordingly included in this volume.

The volatile matter as evolved from the coal is a mixture of fixed gases, vapours, etc., some of the vapours being readily condensed by mere cooling, others being only condensed under conditions difficult to obtain on a manufacturing scale. Some of the latter constituents, however, are soluble in certain liquids. Other constituents, such as ammonia, on being dissolved from the volatile matter, form solutions capable of combining with or dissolving other constituents, so that the solutions obtained are by no means pure.

In general the recovery of the by-products depends on two principles, the first being careful regulation of temperature to bring about condensation of the bulk of easily condensed products, combined with mechanical means for removal of the last traces of such products.

The second consists in bringing the gases into intimate contact with the various solvents used for removal of certain definite constituents. The composition of the by-products is

given at length in later chapters, but the connection between the ultimate analysis of coal and the elementary analysis of the by-products is interesting, and is shown in diagram form in Fig. 1.

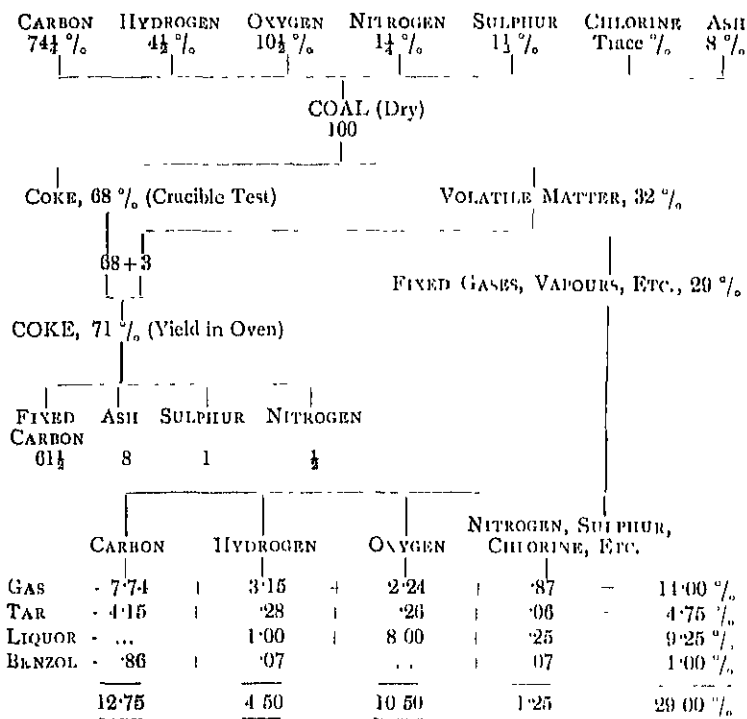


FIG. 1.

The diagram is based on actual analyses and yields at a by-product coking plant in which the coking was carried out at a comparatively high temperature. The difference between the actual yield and the yield in the laboratory is mainly due to decomposition of hydrocarbons from the volatile matter, indications of such decomposition being apparent in the coke. The relatively high content of oxygen in the coal, and consequent high yield of liquor made is obvious, and in the instance given the strength of the liquor was lower than the average obtaining in coke plants generally, but the proportion of

Gas, Etc.	Waste heat	-	-	-	Power.
	Surplus gas	-	-	-	Boilers.
		-	-	-	Gas engines—Power.
		-	-	-	Gas lighting.
TAR	Dehydrated tar	-	-	-	Tar macadam—Road spraying.
	Ammoniacal liquor	-	-	-	See Ammonia.
	Light oil	-	-	-	See Crude benzol.
	Muticle oil	-	-	-	Carbolic acid—Disinfectants—Picric acid—{ Explosives.
		-	-	-	Cresylic acid—Disinfectants.
		-	-	-	Naphthalene—Dyes—Explosives.
	Heavy oil	-	-	-	Creosote oil—Wood preservative—{ Fuel oil.
		-	-	-	Diesel engine.
	Anthracene oil	-	-	-	Naphthalene.
	Pitch	-	-	-	Anthracene oil—Lubricants.
AMMONIA	Sulphate of ammonia	-	-	-	Ammonia soda process.
	Concentrated liquor	-	-	-	Ammonium carbonate.
	Ammonium chloride	-	-	-	Ammonium chloride.
		-	-	-	Liquid ammonia—Refrigerating.
		-	-	-	Ammonium nitrate—Explosives.
		-	-	-	Fertilisers.
CRUDE BENZOL	Washed benzol	-	-	-	Pure benzene—{ Nitro-benzenes—Explosives.
		-	-	-	Aniline—Dyes.
		-	-	-	Perfumes—Flavours—Drugs, etc.
		-	-	-	Motor spirit.
	Washed benzol	-	-	-	Pure toluene—{ Nitro-toluenes—Explosives.
		-	-	-	Toluidine—Dyes.
		-	-	-	Drugs—Saccharine, etc.
		-	-	-	Grease extraction.
SULPHUR COMPOUNDS	Solvent naphtha	-	-	-	Rubber solvent.
	Water-soluble	-	-	-	Terpentine substitute, etc.
CYANOGEN COMPOUNDS	Sulphide of iron	-	-	-	Sulphuric acid.
	Sulphur	-	-	-	Potassium cyanide, etc.

FIG. 2.

nitrogen converted into ammonia was satisfactory. It is scarcely possible to give a distribution chart of this nature in which all the items exactly balance. However, the difference in the totals in this case was very slight, and the allowance for this loss *pro rata* was of little consequence.

In the majority of coke plants the by-products are recovered in their crude state, but the tendency now leans towards fractionation and rectification, increasing thereby the number of products dealt with. The intermediate products obtained are shown in Fig. 2, which likewise indicates their final destination.

CHAPTER II

COOLING AND CONDENSING PLANT

THE gases from a battery of coke ovens or from a section of a battery unite in a collecting main, the individual ovens being connected by means of an ascension pipe and valve (Fig. 3, A),

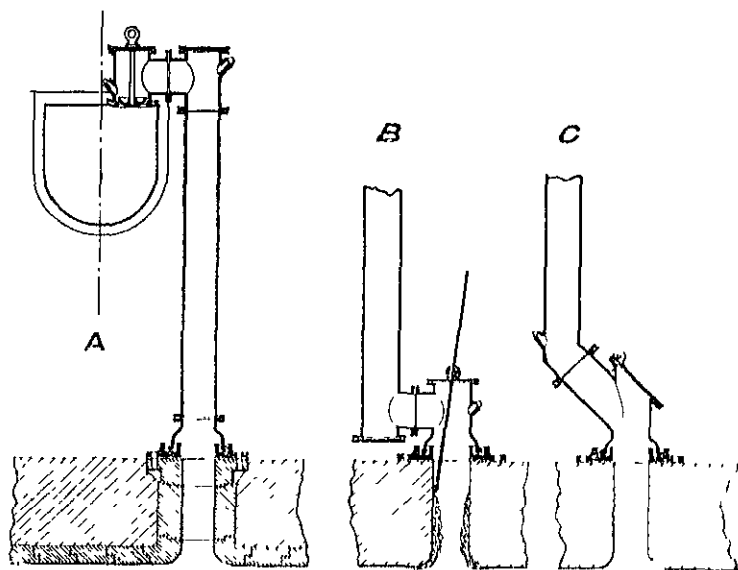
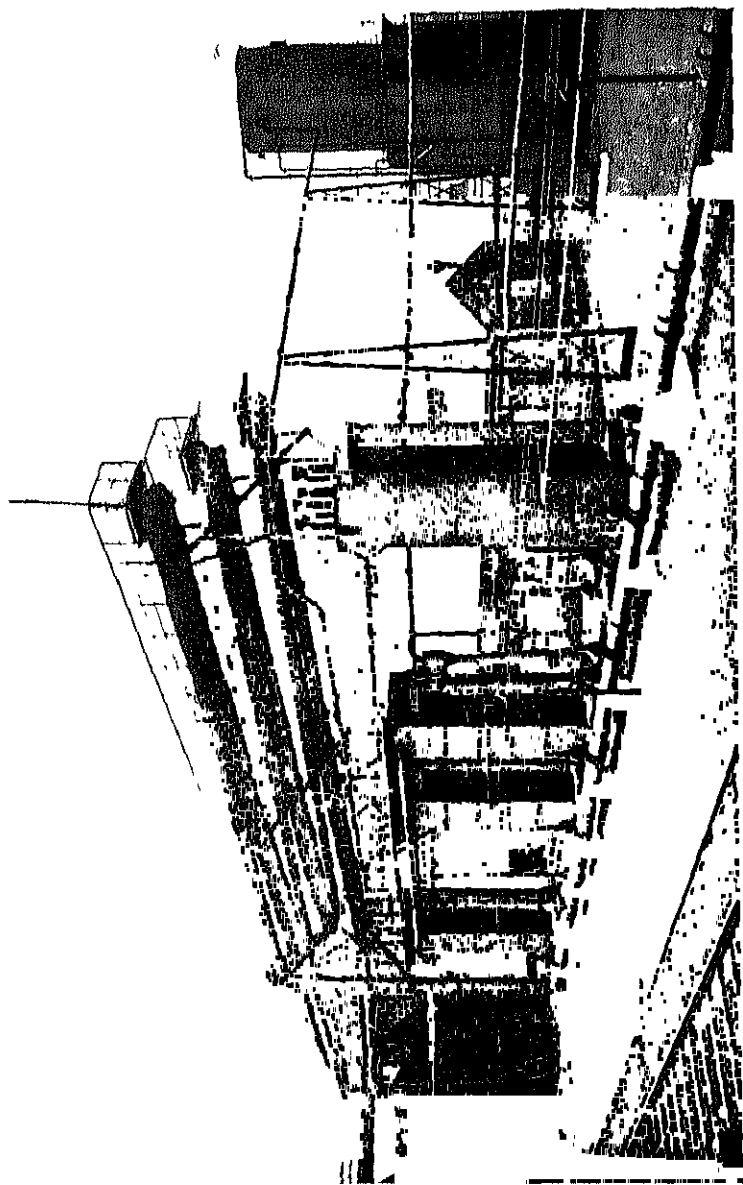


FIG. 3. Types of Ascension Pipes

the latter being in the majority of cases of the mushroom type, although plate valves are occasionally used. The majority of oven builders support this collecting main at some distance above the oven top to secure free access of an all round, utilising the cooling effect of the atmosphere and insulating the main from the heat radiating from the top of the ovens. This, however, increases the length of the stand-pipes, and consequently the difficulty of clearing them of deposited



F O U N D A T I O N L I M E S T O N E Q U A R R Y — O T T O H I G E N S T O K O F F E N

[To face page 7.]

neutralisation of the effect of the heat thus liberated requires the abstraction of approximately four times the number of heat units to be abstracted in cooling the fixed gases. Consequently the area of cooling surface on an average coke works by-product plant should be greater than the figure

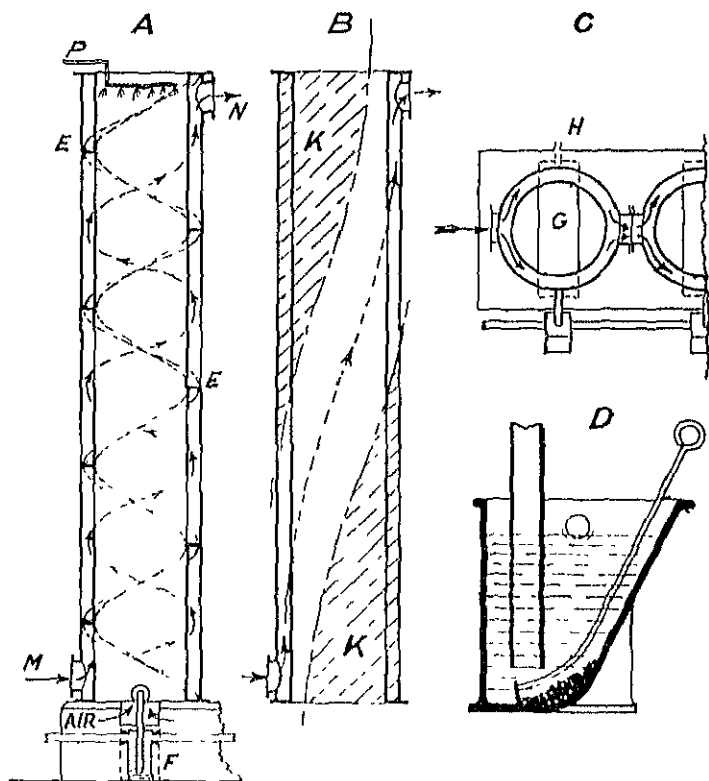


FIG. 5. -Atmosphere Coolers. (Tower type)

usually given in gas works practice, and the writer's experience suggests that in cooling surface calculations an allowance of 60 sq. ft. of air-cooling surface in addition to 50 sq. ft. of water-cooled surface per ton of coal per day is the minimum.

After leaving the collecting main the foul gases are cooled in special apparatus to a temperature controlled by the type

of recovery plant. Thus in direct recovery plants a cooling down to about 80°C . is sufficient, but at the same time the temperature must be brought within sharply defined limits, and in these cases a cooler in which water is the cooling agent is sometimes adopted as the temperature is more easily controlled.

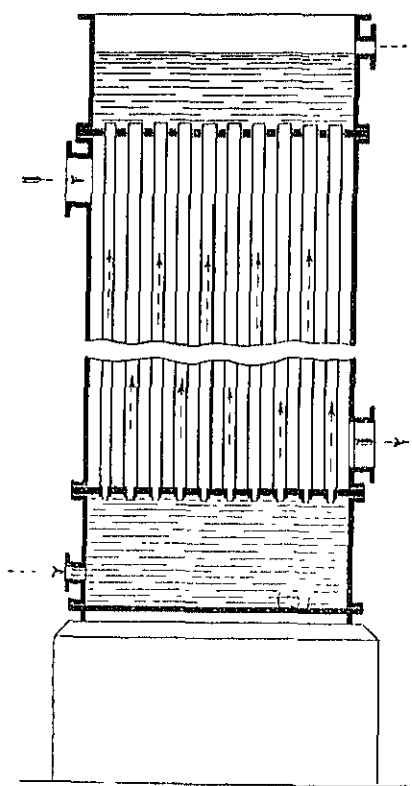


FIG. 8.—Water Condenser.

In the majority of the older plants, and in many semi-direct plants in which the gas must be cooled to about 30°C ., atmospheric coolers are used to bring down the temperature of the hot gases immediately after leaving the hydraulic main, the final cooling being adjusted in condensers of the water-cooled type.

Atmospheric condensers may be of the type shown in Fig. 5, consisting of a vertical cylinder of steel plate surrounding a smaller vertical cylinder. The gas passes through the concentric space as shown. The gas is thus cooled by two surfaces, an inner and outer, whilst additional cooling effect may be obtained

by spraying water on the interior surface. The inner cylinder also acts as a chimney, and an upward current of air is thus generated.

There is a tendency for the gas to take the shortest passage from the inlet to the outlet (shown at B), leaving pockets of stagnant gas as indicated by the shaded portions K. It is therefore an advantage to introduce a spiral baffle, E, to

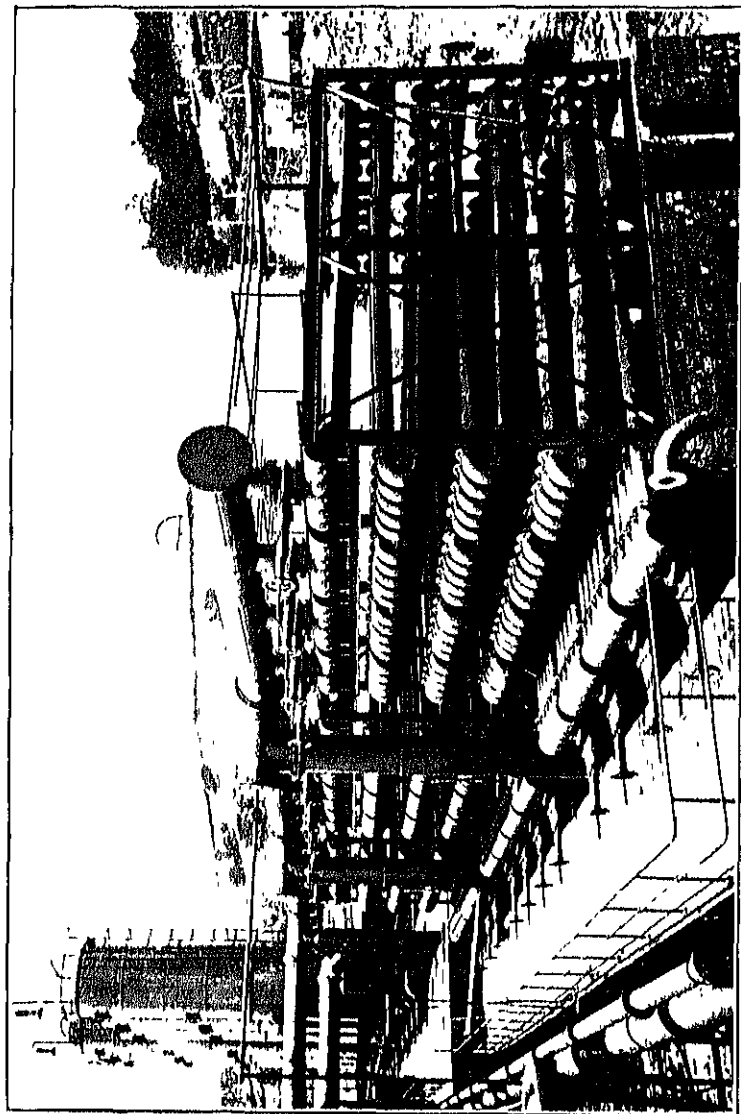


Fig. 1. Schematic diagram of the power plant (Copper type)

and is directed through the series of plates (consisting of one, two, or three pairs) to the upper portion of the apparatus. This apparatus also acts as a governor, helping to maintain a steady pressure. The drum is balanced by a counterpoise, and in case the upper series of perforations becomes clogged with tar or naphthalene the resistance offered would increase the pressure underneath the drum. This would cause the drum to rise, exposing another row of perforations and

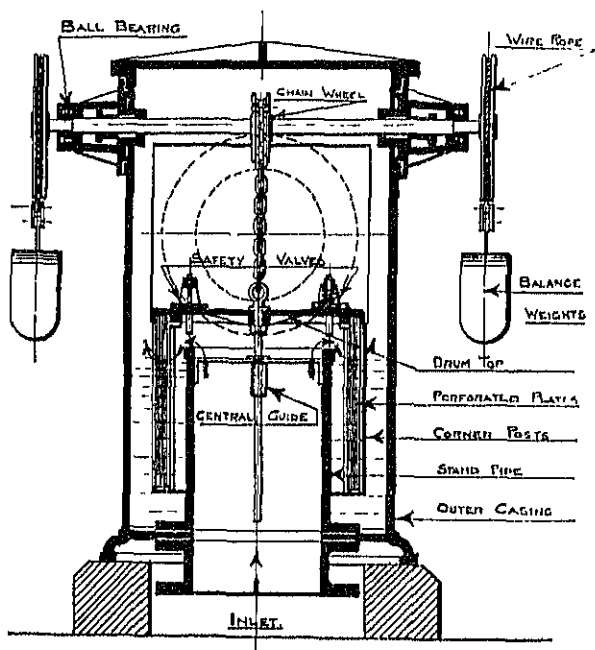


FIG. 9.—Pelouze and Audouin Tar Extractor. (W. C. Holmes & Co.)

relieving the pressure. In case the chain holding up the drum were to break, the above makers have fitted to their machines the relief valves which are opened by contact with projections on the gas passages, the gas then having a free passage to the outlet. In some cases the bell, instead of hanging from a vertical rod, is fixed to a horizontal shaft as in Fig. 10 (Mallet tar extractor). The bell is slowly revolved by the worm gearing as shown, and is washed by contact with the tar collected. A certain proportion of naphthalene is dissolved

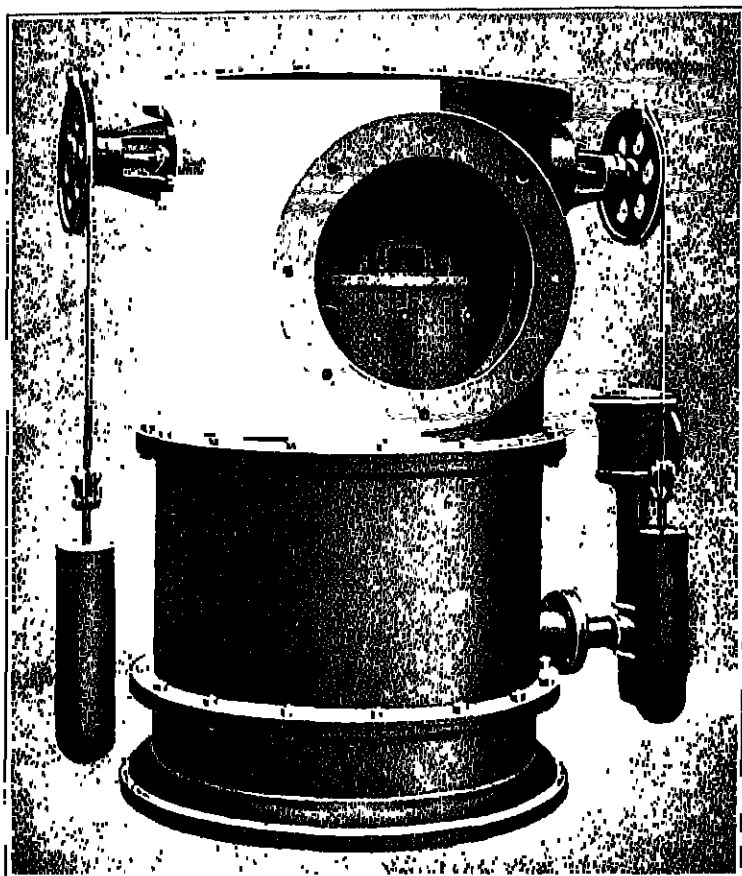
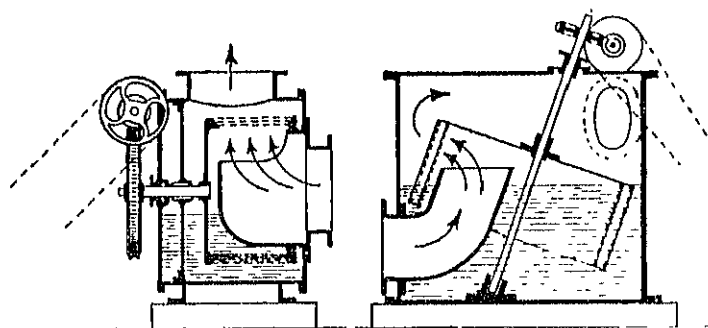


FIG. 92. IMPROVED OAK EXTRACTOR. (W. C. Holmes & Co.)



in this manner, and the apparatus will work for a longer period before it is necessary to clean it by by-passing and steaming. Fig. 11 shows an apparatus designed on similar lines to the Mallet, the rotary shaft in this case being inclined. Having thus dealt with the tar, there still remains ammonia to be dealt with. A large proportion of ammonia has already been removed in the air and water coolers, and in the tar extractor if a "bubble" type is used for the latter. The removal of the last traces of ammonia is carried out on certain definite principles, depending mainly on the solubility of ammonia in water. In the first place the temperature of the water used and of the gas treated must be low, usually not



FIGS. 10, 11. — Tar Extractors

more than 25° C. The figures below show the effect of temperature on the solubility of ammonia in water

Temperature Deg. C.	Grams Ammonia Absorbed by 1 gm. Water
10	679
20	526
30	403
40	307
50	299

In the second place the amount of water used is important, since it serves to dilute the liquor ultimately arriving at the sulphate house. A weaker liquor requires a greater consumption of steam in that department, and if dilution is carried to excess, difficulties in manipulation of the sulphate or concentrated liquor plant will arise. It is therefore

obvious that contact between gas and water must be as efficient as possible. The efficiency depends on the mechanical means for ensuring contact and on the duration of contact. Washers of the "bubble" type might be used, but the high resistance offered usually presents too great a drawback.

Water sprays with suitable precautions may be used, or films of water induced by centrifugal action. Washers of this type, whilst occupying less space and being intensive in action, require mechanical energy either by pumping or by rapid revolution of a shaft and appliances attached. Surface contact is largely utilised, and in this case the aim of the designer is to secure a material which offers the greatest surface in a unit bulk.

In the earlier types coke was used, but wooden boards set on edge represent recent practice. Surface contact apparatus may be divided into two classes, stationary or tower scrubbers and rotary scrubbers. Fig. 12 shows a modern arrangement of tower scrubbers. These consist of two vertical cylinders A, of cast-iron or steel plating filled with packing as shown at B, supported at various points M by angle irons or brackets, etc. The packing in this case consists of boards, six inches wide, five-eighths of an inch thick, set on edge, and half an inch apart. Alternate layers are set at right angles to each other as shown, whilst in some cases the lower edge is serrated to distribute the falling liquid more evenly over the succeeding layer. Water is carefully distributed over the whole area of the uppermost layer from the main C by various devices, such as jets playing on flat plates, etc. It is highly important that these jets, etc., be easily accessible for cleaning, as even distribution of washing liquid is a primary essential. Gas enters at the base, and flows in opposite direction to the liquid.

Tower scrubbers should be tall and narrow, rather than short and wide, to lessen the tendency of the gas to take a selective path, the height being roughly seven times the diameter. A surface contact scrubber of the rotary type is shown in Fig. 13 ("New" washer scrubber, W. C. Holmes & Co., Huddersfield). The chamber in this case is horizontal, and is divided into sections as shown. In each section is a circular plate E attached to the main shaft by a cast-iron

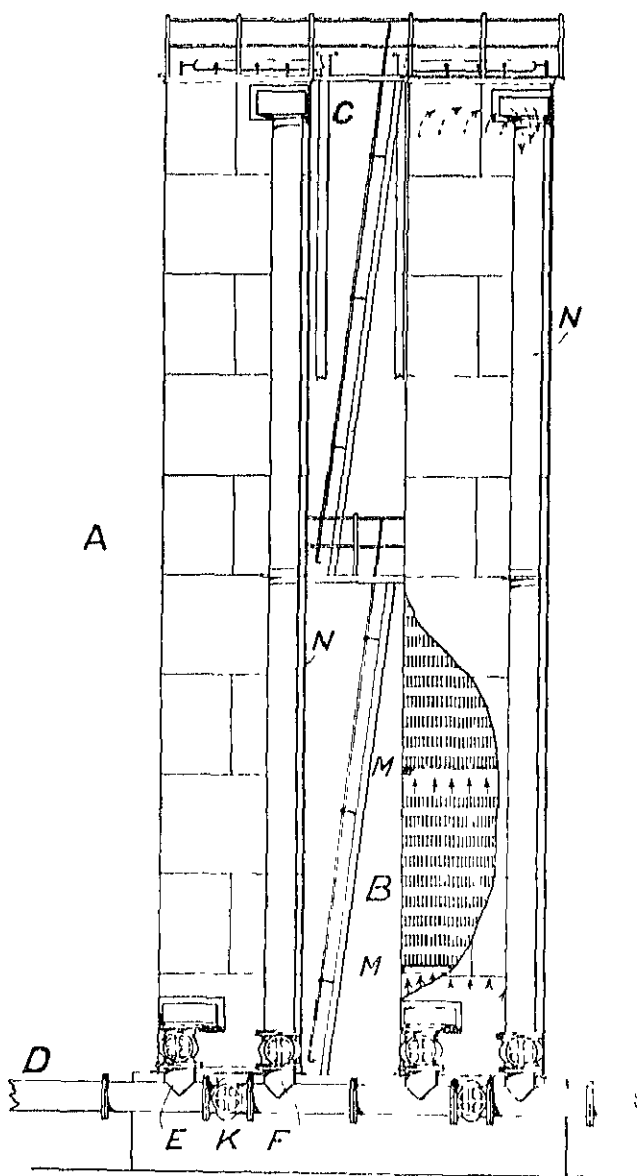


FIG. 12.—TOWER SCRUBBERS

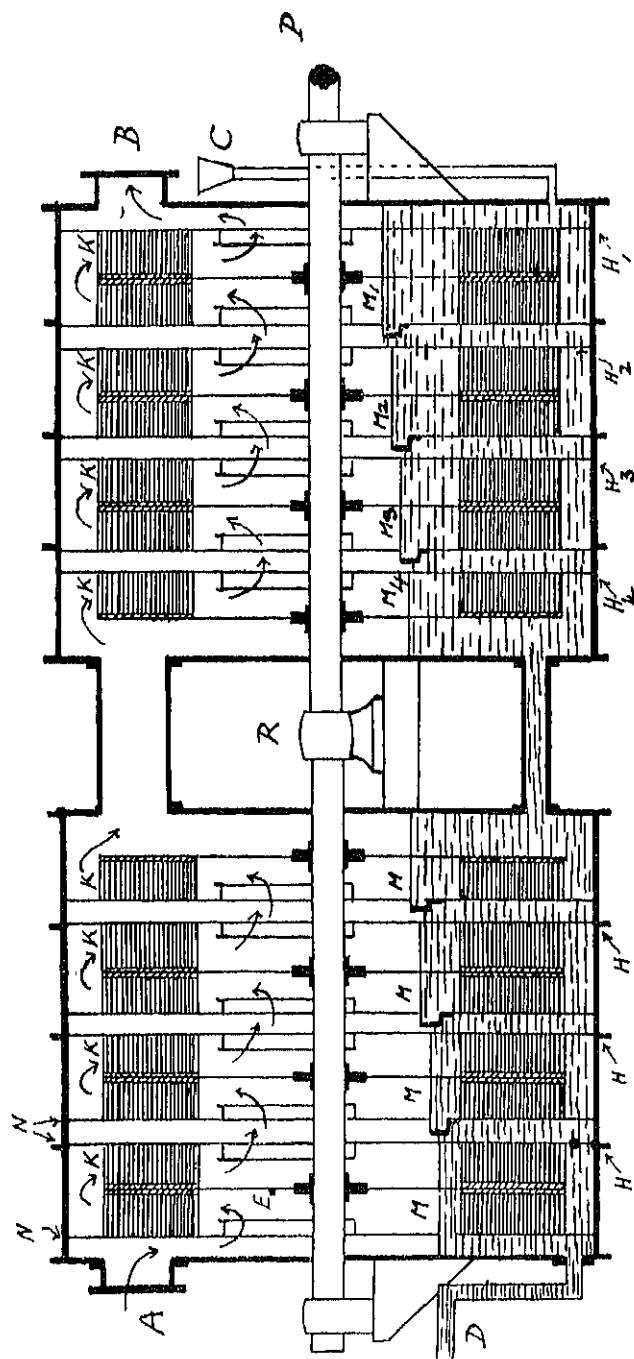


FIG. 13 —REVOLVING WASHER SCRUBBER. (W. C. Holmes.)

boss. To each side of this plate a series of brushes K is fitted radially, the brushes forming a close fit between the plates N of each section. The gas is thus compelled to pass upwards on one side of the plate, and downwards on the other, through the interstices of the brushes.

These brushes, passing through the liquor M in the lower portion of the scrubber, are kept moistened, and thus the condition of the intimate contact with wetted surface is secured. Water is fed into the chamber at C , and passes through the successive sections by means of inlets II_1, II_2, II_3, II_4 , etc., and overflows M_1, M_2, M_3, M_4 , etc., finally leaving the scrubber through the seal D . Thus the washing medium is passing in opposite direction to the gas, which is thus purified in stages, the final washing being with the weakest liquid. This counter-current principle is important, and is made use of in all recent types of scrubbers. Other types of rotary scrubbers are worked on the same principle, but with different packing material, wooden balls, thin metal plates in bundles, or canvas screens being used for this purpose. An example of the centrifugal type of washer is shown in Fig. 14.

This example consists of a series of superimposed washing chambers A . The washing medium is introduced at D , and passes successively through each chamber. The driving shaft is vertical, and is actuated by bevel gearing at B . A distributing device for each chamber is attached to this shaft. The device consists of a dish with perforated sides as shown, to which is attached a series of pipe bends dipping below the surface of the liquor. The revolution of the shaft causes

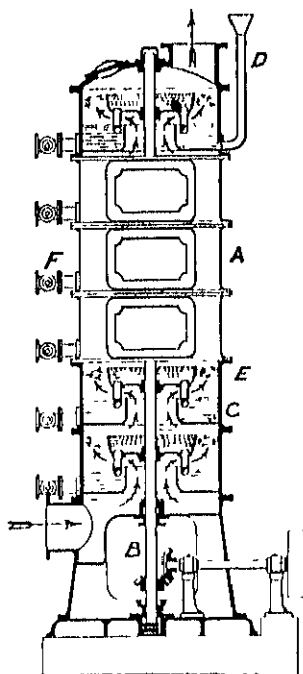


FIG. 14. Centrifugal Washer
(Kukhan, Hulett & Chandler.)

the bends to scoop up a supply of liquor, which is then energetically sprayed by means of the perforations and centrifugal action. The liquor in the form of a series of films or sheets passes right across the intervening space to the outer casing as at E. The gas must pass through these films, and if the supply of liquor and the speed of the shaft is maintained there is no opportunity of "slip."

An intensive type of scrubber designed by the writer is shown in Fig. 15. In this apparatus, which is also suitable for tar extraction, the principle of a liquor spray with certain modifications is utilised. The use of a spray *per se* is by no means novel, but the main object of this invention is to bring the gas into close proximity to the points of generation of the sprays, thus utilising the portion in which the liquid is at its highest velocity. For this reason the gas is subdivided into a series of comparatively narrow concentric passages, across which the jets of liquid are thrown. In this apparatus the units (one of which is shown on an enlarged scale) consist of an inner liquor distributing tube B and an outer controlling tube C. A mere tightening of the cap D secures both tubes in position, and as one end only is connected with the body of the chamber, the unit as a whole is free to expand or contract. The distributing tubes are connected to a common chamber M, fed by a pump, and are drilled so as to provide any desired number of sprays as at E, in addition to the external spray from the cap D. The total area of concentric passages is designed to be approximately equal to the area of the main gas inlet, so as to equally distribute the gas amongst the several units. The action of the washer is as follows. Gas enters the apparatus and passes upwards in the various concentric passages. Here it is cooled by contact with the tubes B, all filled with circulating washing liquor, and brought into active contact with the liquid by the mechanical action of the sprays at E. On reaching the tops of the tubes the gas then enters the space K surrounding the external tubes and passes downwards to the gas outlet. As this space is also constructed, the gas is forced into contact with the whole of the exterior surface of the controlling tubes C. The sprays in the caps D and the grooves F ensure an equal distribution of the washing medium

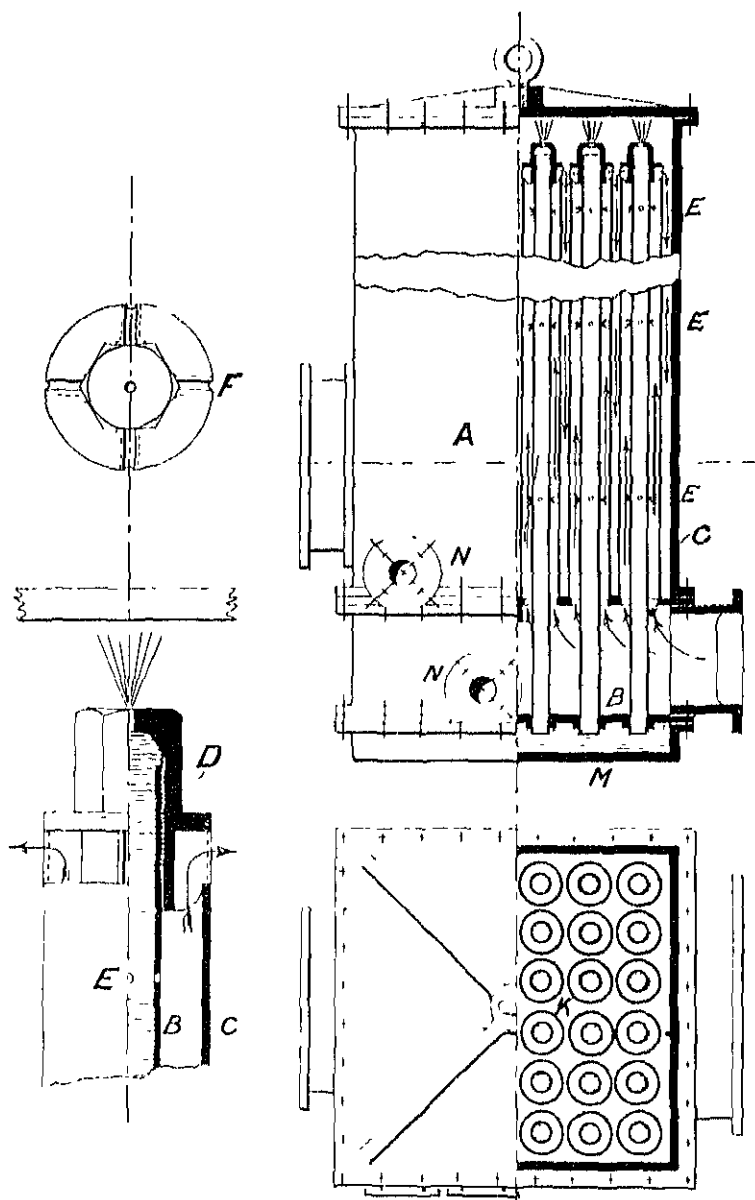


FIG. 15. INTENSIVE SPRAY WASHER. (R. & J. Dempster, Christopher's Patent.)

over the surface, so that we obtain here the conditions of good surface contact, whilst any liquid carried over mechanically from the inner sprays has an opportunity of separating from the gas. The washing medium is run off from the outlets N through a common seal pot. The liquor and tar from the various sections of the by-product plant are usually conducted to some type of separator in which the tar sinks to the bottom, the ammoniacal liquor remaining on the top. The products are then run off at different levels or pumped into their respective storage tanks. In handling the ammoniacal liquor it is advisable to avoid any unnecessary exposure to the atmosphere. Some of the overflowing liquor, as for instance from the hydraulic main, is at a fairly high temperature, and the loss due to volatilisation of ammonia is appreciable and at times severe. The writer has experience of a decided advantage in substituting a closed tank for an open type of separator. Where it is desirable to have overflows under visual observation, it is advisable to introduce special bends with faced inspection flanges, which may be weighted and hinged to allow of easy access. The question is of considerable importance, and has been dealt with at some length in the Annual Reports for 1914 and 1915 of Mr W. S. Curphey, Chief Inspector under the Alkali Works Regulation Act. The results of several interesting experiments are given, showing the advantage of covering in all seal pots and siphons, and the beneficial action of a superficial film of mineral oil as a protective layer in liquor storage tanks. The report also deprecates the practice of delivering liquor into tanks from pipes allowing the liquor to fall through the air, and recommends the lengthening of such pipes so as to seal the ends in the liquor.

CHAPTER III

GAS EXHAUSTERS

THE gas exhauster has been described as the heart of a gas works, and the title applies with equal force in the case of a modern coke plant. The usual coolers, washers, scrubbers, etc., offer, in total, considerable resistance to the passage of the gas, and it is the duty of the gas exhauster to overcome this resistance. In some of the more recent types of ammonia recovery plant the gas is forced through a bath of sulphuric acid in addition, thus increasing the work of the exhauster. By the mechanical assistance of the exhauster the gases and vapours, etc., should be conducted from the coking chamber as quickly as they are evolved. If the suction due to the exhauster is not sufficient to remove these gases a pressure in the coking chamber is developed, and the gases tend to "short circuit" themselves, through leakages, into the side flues, the action being intensified by reason of the slight suction in these flues. If the oven walls are tight there is still the risk of the gases escaping through the luting of the oven doors, and in any case there is a positive loss of gas and by-products. On the other hand too great a suction from the exhauster tends to draw in air through the luting of the doors, the effect in bad cases being seen in an overheated crown of the oven, decomposition of some of the by-products, and deterioration in the quality of the gas. In general it is advisable to work the exhauster at such a speed as to secure a "level gauge" at the ovens.

Various types of exhausters are used, such as jet exhausters, positive or rotary exhausters, and centrifugal turbo-exhausters. The jet exhauster (Fig. 16, *F*) has the advantage in the absence of moving parts and in compactness, but it has an attendant disadvantage in the large volume of steam actually introduced into the gas, necessitating condensation

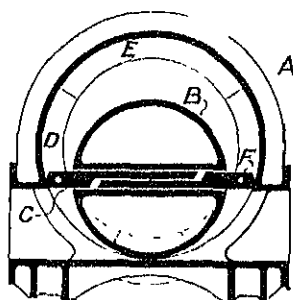
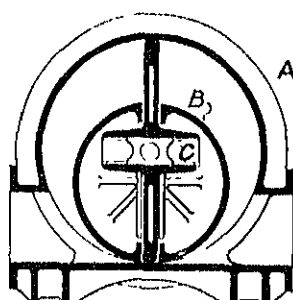
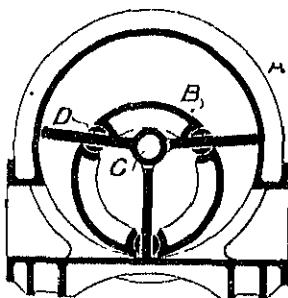
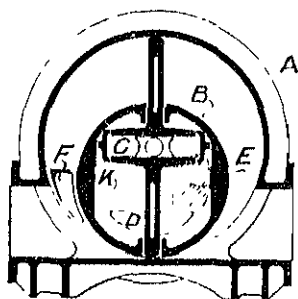
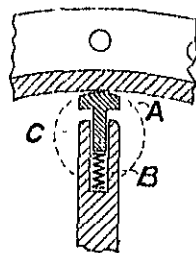
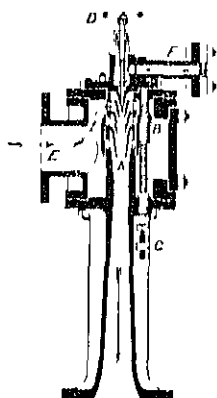
**A****B****C****D****E****F**

FIG. 16. - TYPES OF LAMASTERS.

and removal at a later stage. The suction is built up in a series of nozzles A, being primarily induced by the steam introduced at F, and controlled by the needle valve D. A sleeve B, regulated externally by the position of the indicator C, serves to cut out or throw into action a series of openings according to the volume of gas to be dealt with. The gas enters at E, is trapped by the expanding jet of steam, etc., and leaves the apparatus as shown.

The rotary exhausters may be said to have sprung from two early types of machines, the Beale exhauster and the Roots blower. The Beale type consists of an outer casing and an inner drum, the latter serving as an axle to drive various forms of blades in such a manner as to sweep through the crescent-shaped space between the drum and casing. As the blade revolves it forces the gas forward to the pressure side and creates a partial vacuum on the suction side. The drum serves two purposes: it drives forward the blades and acts as a non-return valve to prevent gas from the pressure side passing back to the suction side. The earliest type of the Beale exhauster is shown in Fig. 16, *A*. In this machine the slide C, passing through the axle B, was guided by blocks D running in a recess E in the end plate. The pins F rotating with the blocks D served to maintain rubbing contact between the slide and the outer chamber. The slide was in two portions, carefully machined and sliding over each other in the slot in the axle. The guiding blocks in this case travelled at a high linear speed, giving rise to considerable friction. This defect was remedied in the later Beale exhauster manufactured by the Bryan Donkin Co. (Fig. 16, *B*). In this the guiding of the slide motion is brought to the centre by using a block C running on a pin fixed in one of the end plates. The slide is cast in one piece, and the block provided much larger wearing surfaces as compared with the older guiding rings. In addition, the high linear velocity of the circumferential guiding blocks is avoided, the relative velocity of the block C being reduced to only a tenth of that obtaining in the original type. The internal friction is so much reduced that the power required to drive the exhauster has been reduced by 25 per cent. The chamber is bored to the exact oval shape described by the motion of the blades, the vertical

diameter being equal to the chord passing horizontally through the centre of the axle B. The axle is cast in one with the driving shaft, and just clears the bottom of the chamber, the non-driving end running in a race in the end plate, the inner diameter of the race forming a bearing easily lubricated. The slide is entirely supported by the block C, the only pressure on the chamber being due to the springs B (Fig. 16, E) under the packing strips or nose-pieces A, which ensure efficient contact and hence a minimum of "slip." A modification,

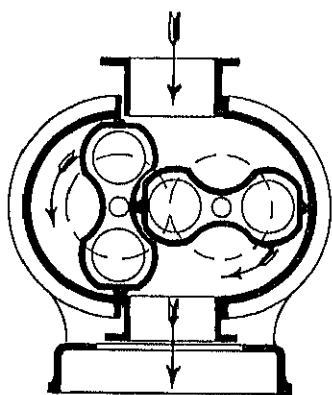


FIG. 17.—Exhauster, Roots Type.
(Messrs Thwaites Bros.)

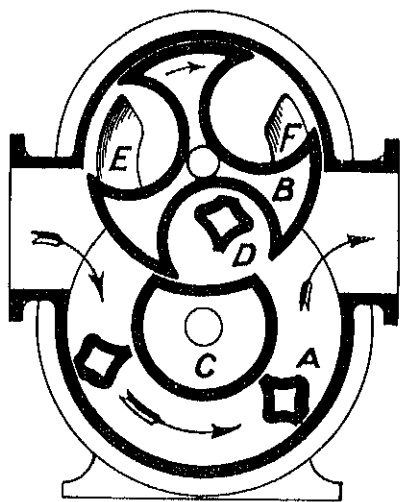


FIG. 18. Sturtevant Gas
Exhauster

designed by Mr Bryan Donkin, is shown in Fig. 16, D, in which the motion of the slide in the hollow axle is utilised to increase the volume of gas dealt with. On each of the end plates ports as at F and E are fitted, forming connections with the interior of the drum and the suction or pressure side of the exhauster. Openings D in the end of the axle pass the ports at definite intervals; each revolution and the movement of the slide between the machined faces K alternately draws in gas from the suction port F, and expels it through a port in the end plate (not shown on the drawing) to the pressure side. The capacity is increased, but at the cost of additional working parts, and many engineers prefer the ordinary central

guided exhauster on this account. Fig. 16, *C* shows a type of exhauster fitted with three blades. The increase in the number of blades tends to secure a steadier gauge on slow speeds. For larger units four blades are used, the principle being the same. In these three and four blade exhausters the outer chamber is bored to a true cylinder. The blades are supported by a central pin *C* secured in a deep boss in the end plate. The axle is fitted with three or four rollers *D*, oscillating in bearings and slotted to receive the slides. The rotation of the axle *B* thus carries round the various blades, and the gas is swept round the space between the inner drum and the outer chamber to the pressure side. An exhauster of the "Roots" type, as manufactured by Messrs Thwaites Bros., Bradford, is shown in Fig. 17. In this case two hollow impellers of cast iron or cast steel revolve simultaneously in opposite directions in a casing as shown, synchronism being secured by spur gearing. The impellers are of carefully designed shape, the tip of either impeller engaging in the indented portion of the other impeller in such a manner as to avoid undue slip. As a rule this type of exhauster is fixed as shown, but occasionally the inlet and outlet passages are set horizontally, in which case the axes of the impellers are set in a vertical plane.

The Sturtevant exhauster (Fig. 18) consists of two accurately bored cylinders partly intersecting, on either side of which are the intake and discharge openings. Inside the casing are two rotors, an impeller which does the real work of exhausting and an idler which acts as a non-return valve. The impeller consists of three diamond-shaped blades *A*, joined together by a central web, and actuated by a central driving shaft. The blades revolve in the space between the casing and a stationary core *C*, and the gas is conveyed from the inlet to the outlet as shown by the main arrows. The idler *B* is revolved at the same speed as the impeller by means of cut spur gearing, and is shaped so as to trap the blades of the impeller as shown at *D*, thus preventing any escape of gas from the pressure to the suction side of the exhauster. Any gas left under the pressure in *D* is by-passed by means of one or other of the leakage chambers *E* and *F* fitted in the end plate. These leakage chambers make it possible to recover the pressure which

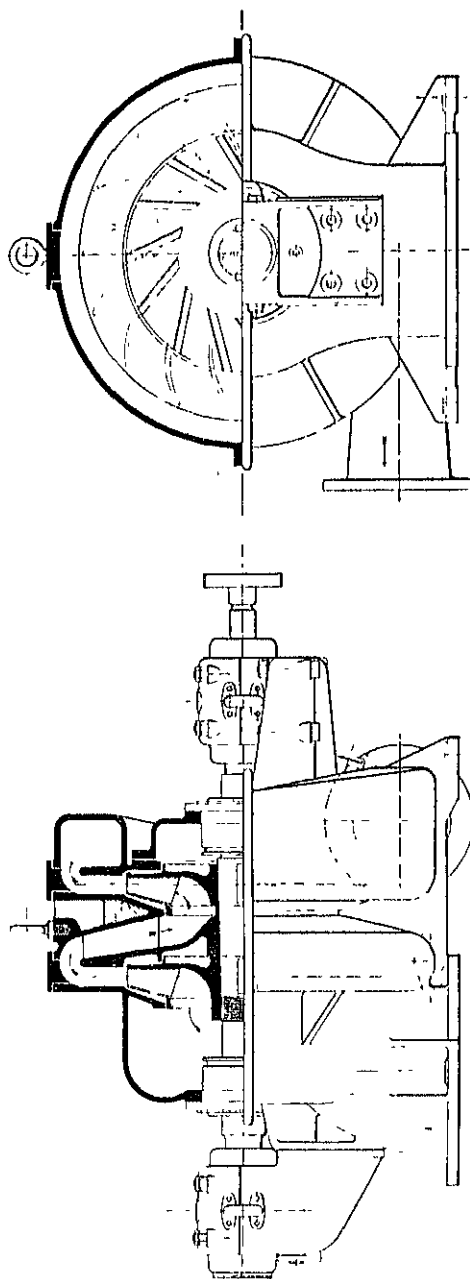


FIG. 19 —TURBO-EXHAUSTER. (The Bryan Donkin Co.)

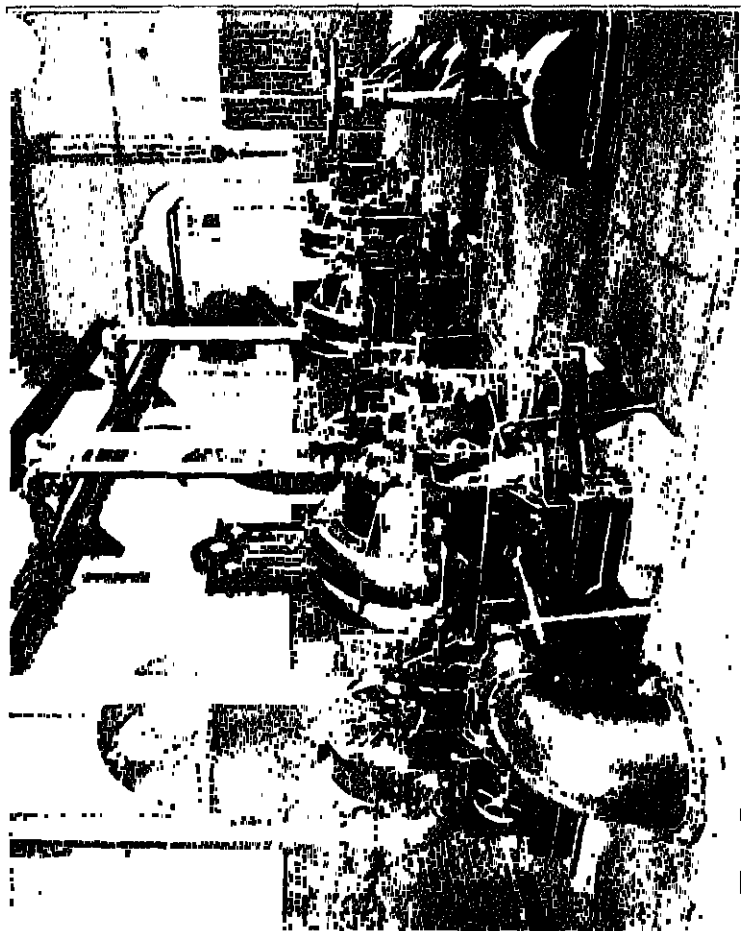
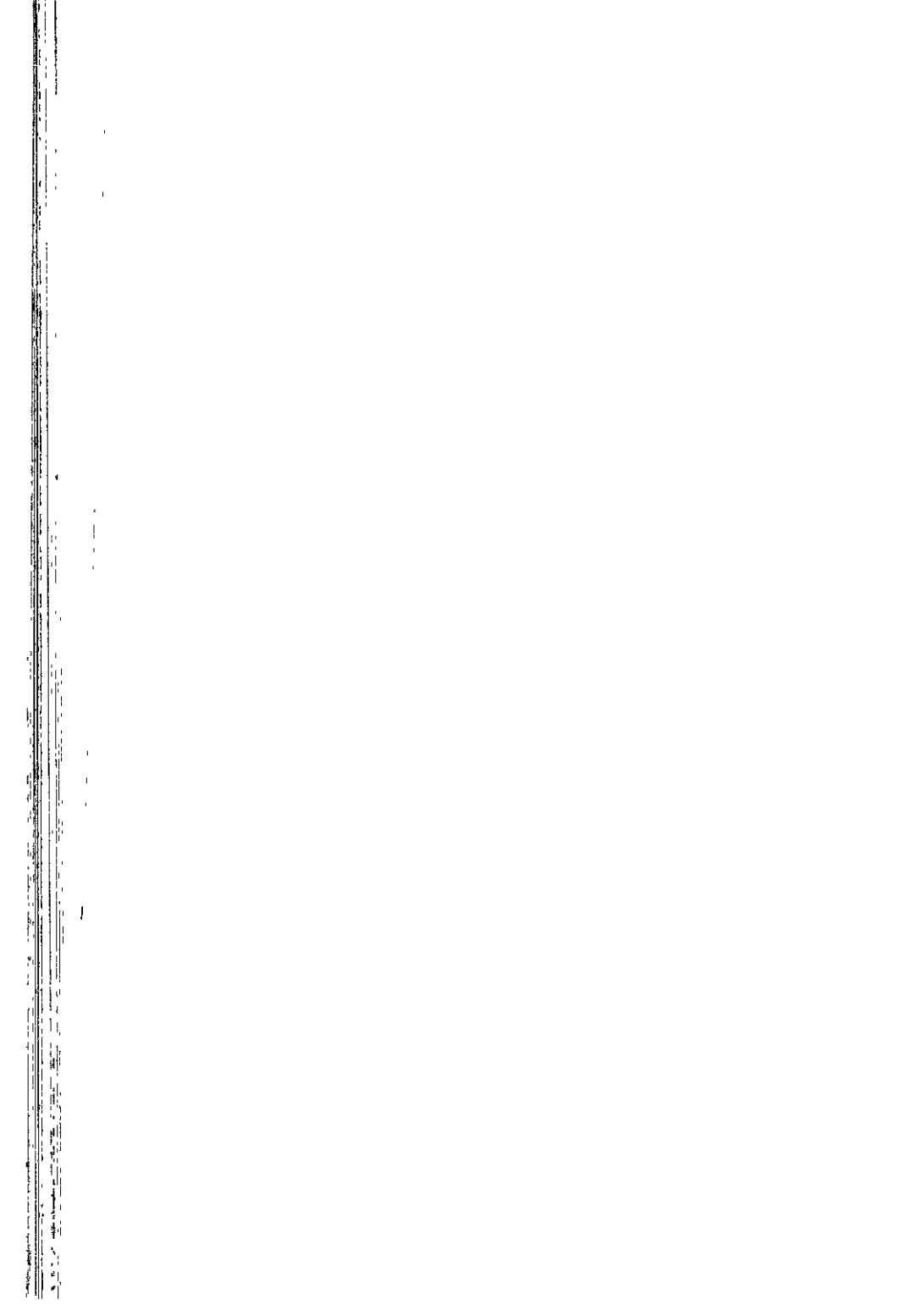


Fig. 20. The Engine of the Boston Docking Co. (Station Carves Ovens.)



otherwise would escape from the idler pockets, thus increasing the efficiency and decreasing the noise. The idler itself does not assist in exhausting the gas, and consequently requires little power for its rotation, whilst the space between the idler and the impeller is such that no amount of wear will allow the rotors to come in contact, thus permitting a high speed of rotation. A type of exhauster which has come into prominence during recent years is the turbo-exhauster. Owing to the high velocity the dimensions are considerably reduced and the exhausters occupy very little floor space as compared with exhausters of the Beale type. They have an advantage in the shape of larger clearances and no rubbing surfaces, and appear particularly suitable for direct ammonia recovery processes. Figs. 19 and 20 show a Bryan Donkin two-stage turbo-exhauster. The inlet and outlet branches are fitted to the lower half of the casing to allow easy access to the impellers without interfering with any pipe joints.

CHAPTER IV

COMPOSITION AND ANALYSIS OF AMMONIACAL LIQUOR

THE liquid from the various washers, coolers, etc., is a mixture of tarry and watery constituents. The nature of the tarry compounds from any unit varies according to the relative situation of such unit in the recovery system, and is dealt with in a later chapter. The primary source of the other constituents is the liquid condensed from the vapour arising from the water of formation of the coal, and from the water mechanically introduced in the coal washing. This water dissolves a proportion of ammonia from the foul gases varying with the temperature of any particular condenser. A solution of ammonia is thus formed, but as other bodies having a strong affinity for ammonia are also present in the gas, the liquid becomes a complex mixture of compounds of ammonia. Some of these compounds are readily decomposed by mere heating, whilst others are more stable, and require, in addition to heat, the presence of an alkali, such as soda or lime, to bring about decomposition. The ammonia existing in the former condition is known as "free" ammonia, and in the latter as "fixed." The various compounds usually associated in ammoniacal liquor are:—

Free	{	Ammonium carbonates.
		„ sulphides.
		„ cyanide.
Fixed	{	Ammonium chloride.
		„ sulphate.
		„ sulphite
		„ thiosulphate.
		„ sulphocyanide
		„ ferrocyanide

The specific gravity of the liquor is about 1.05.

The compounds above mentioned are produced in various ways.

Carbon dioxide is always a constituent of the gases coming from the ovens, and is formed by the union of some of the carbon of the coal with oxygen derived from the air which is unavoidably admitted with the slack during charging. When ammonia gas comes in contact with carbon dioxide below a certain temperature, one or other of the carbonates of ammonia is formed according to prevailing conditions.

The carbonates are white solids, which, however, cannot exist at high temperatures, and are consequently not formed until below a certain temperature.

The carbonates of ammonia smell of free ammonia under ordinary atmospheric conditions, probably through the action of carbon dioxide from the air, partly due also to the presence of carbamate, since this compound is formed by the interaction of gaseous ammonia and carbon dioxide, if these are dry and not too hot.

Ammonium Sulphide is produced by the action of sulphuretted hydrogen on ammonium hydrate, the former having been derived from the sulphur contained in the iron pyrites always associated more or less with coal. There are several sulphides of ammonium, containing variable amounts of sulphur. It is to the presence of these compounds that the disagreeable smell of the gas liquor is chiefly due. All the sulphides give insoluble precipitates with lead and zinc salts, and on this reaction may be based a method for their estimation. They easily decompose, and are volatile on heating.

The sulphocyanide of ammonium is formed by the union of hydrocyanic acid and ammonium sulphide. It is possible also that carbon disulphide takes part in the formation.

Sulphite of ammonium is produced by the union of sulphur dioxide, derived from the pyrites in the coal, and gaseous ammonia, in a similar manner to the formation of carbonate. The sulphite, in presence of free sulphur, forms hyposulphite or thiosulphate.

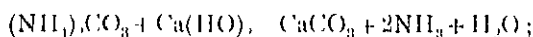
Ammonium Chloride is derived from sodium chloride, or common salt, in the coal, and varies considerably with the class of coal used. Some coals contain a fairly large amount of salt, others are practically free. Ammonium chloride,

commonly known as "sal ammoniac," is a white solid which readily sublimes, and easily dissociates into ammonia gas and hydrochloric acid gas.

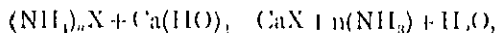
Free Hydrocyanic Acid is the result of the direct union of carbon and hydrogen with nitrogen at the high temperatures used in coking, so that a portion of the total nitrogen of the coal is thus changed, and not recovered as ammonia.

Treatment of Ammonia Liquor.—Although ammonia liquor is thus shown to be such a complex solution, fortunately all the compounds are amenable to one form of treatment. When the liquor is brought into contact with milk of lime (chemically calcium hydrate), all the ammonia is driven off in the form of free ammonia or ammonia gas. This reaction is brought about in the "stills," which are fully described in a later chapter.

A typical equation for the reaction is as follows:—



or generally expressed:—



where X represents the acid radicle.

As the terms "free" and "fixed" ammonia are often used in speaking of ammonia liquor, it will be well to understand what is implied by them.

The "free" ammonia is that which is given off from the liquor by boiling only, without the addition of an alkali or base, such as soda or lime.

The "fixed" ammonia is that which is not driven off by simply boiling, unless an alkali or base be present in moderate excess. In the "stills" of a recovery plant lime is used. This causes the decomposition of the whole of the ammonium compounds, and the liberation of all the ammonia in the free, gaseous condition, ready for absorption in the sulphuric acid, when it again becomes "fixed" and converted into ammonium sulphate.

Valuation of Ammonia Liquor—An approximate idea of the strength of ammoniacal liquor may be obtained by means of a Twaddell or other similar hydrometer, but to ascertain the exact amount of ammonia present a chemical test is necessary.

An estimation of the *total* ammonia is usually made, that is the free and fixed together, and this is done in the following manner:—

Having obtained a representative sample, 10 c.c. are measured off and transferred to a small flask, to the neck of which a rubber stopper has been previously fitted. Through this stopper is a glass tube, bent twice at right angles and connected to a bulb U tube as shown in Fig. 21. Into the bulb U tube is measured 10 c.c. of normal sulphuric acid, that is, of such strength that each cubic centimetre contains 0.49 gm. of sulphuric acid or 49 gm. per litre. A moderate excess of a strong solution of sodium hydrate (caustic soda) is now added to the flask, and the stopper quickly replaced, gentle heat being then applied to the contents of the flask, gradually increasing it so as to maintain a gentle boil for about half an hour. By this means the whole of the ammonia is distilled over into the acid with which it combines, forming ammonium sulphate, and neutralising a proportional amount of the free acid. It then remains to carefully detach the U tube and its contents, and transfer the solution to a glass beaker or porcelain basin, the latter preferred, rinsing out the tube with distilled water several times, care being taken to avoid any loss by splashing, etc. It is now necessary to estimate how much of the acid has been neutralised by the ammonia which has passed into it. This is done by adding two or three drops of a solution of methyl orange to the liquid in the basin, and then adding carefully a normal solution of sodium carbonate or hydrate until the pink colour of the solution is changed to yellow. The end reaction is very distinct, and indicates exactly when the remaining excess of acid has become neutralised by the standard solution of soda. Each cubic centimetre of normal sulphuric acid neutralised by the ammonia which has been liberated from the 10 c.c. of ammoniacal liquor, represents 0.17 gm. of ammonia (NH_3).

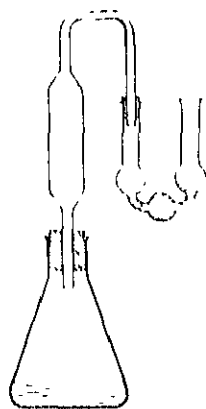


FIG. 21. Apparatus for the Estimation of Ammonia.

An example of the figures in an actual test will no doubt make the process more comprehensible:—

10 c.c. $\frac{N}{H_2SO_4}$ originally used in U tube.

3 c.c. $\frac{N}{NaHO}$ required to neutralise after distillation is complete.

$10 - 3 = 7$ c.c. $\frac{N}{H_2SO_4}$ neutralised by the ammonia from 10 c.c. of ammonia liquor,

and each c.c. sulphuric acid neutralised = 0.17 gm. ammonia (NH_3). $\therefore 7 \times 0.17 = 1.19$ gm. ammonia from 10 c.c. of ammonia liquor, and hence 1.19 per cent. ammonia (NH_3).

If it is desired to estimate the free ammonia and the fixed ammonia in a liquor, separately, a measured quantity is taken as before, and distilled over into a known volume of standard acid, *without adding sodium hydrate* to the solution in the flask. On titration with standard soda as before, the figure obtained gives the free ammonia only. This amount deducted from the total ammonia, as determined by a separate test, represents the ammonia in the fixed condition.

Concentrated Liquors.—In many plants, instead of recovering the ammonia in the form of sulphate, it is concentrated in the form of liquor and sold as such. The strength of such liquor varies from 15 to 20 per cent.

The liquor may be tested by the hydrometer as to its strength, but it is preferable again to use a chemical method. It is found that with fresh liquor it is sufficiently accurate to titrate direct with normal sulphuric acid, that is, without having to distil with caustic soda. If, however, the liquor is a few days old it is necessary to distil with soda into normal acid as described in the testing of ammoniacal liquor, otherwise too low a result is obtained. In dealing with a liquor so strong as concentrated liquor usually is, it is either necessary to determine its specific gravity by means of the specific gravity bottle (see p. 29, Vol. I.), or to actually weigh the liquor used in the estimation. This latter is preferable, and may be carried out as follows. Weigh a small conical glass flask containing a few cubic centimetres of distilled water, then

add *about* 5 c.c. of the concentrated liquor whose strength is to be determined, and weigh again, having stoppered the flask up with a cork and rubber tubing on which there is a spring clip. By this means the *weight* of the liquor used is ascertained. This is then distilled with excess of caustic soda into about 50 or 60 c.c. of normal sulphuric acid, carefully measured of course. Gradually warm up the flask and contents and distil at a brisk boil for about twenty minutes. Each cubic centimetre of normal sulphuric acid neutralised represents '017 gm. of ammonia (NH_3). It may be explained that when dealing with an ordinary ammoniacal liquor, say of 1.0 to 1.5 per cent. strength, it is sufficiently accurate to *measure* the 5 or 10 c.c. taken for analysis, and to take it that this volume weighs 5 or 10 gm., as the case may be. But in a highly concentrated liquor containing from 16 to 20 per cent. of ammonia it would be misleading to do this, and consequently it is necessary to weigh the portion taken, or to determine the specific gravity of the liquor, and from that calculate the weight of any measured volume dealt with.

Estimation of Total Sulphide in Liquor.—The principle of this estimation is based upon the fact that when a solution of zinc chloride (ammoniacal) is added to the ammonia liquor the sulphides are precipitated as zinc sulphide. The solution is boiled up, and after settling, the precipitate is filtered off and washed several times with hot water, and finally titrated with a standard solution of iodine, decinormal strength, whereby the amount of sulphur in the form of sulphide is readily calculated. Every 97 parts of zinc sulphide are equivalent to 32 parts of sulphur or 31 parts of sulphuretted hydrogen.

An example of this method is given in the Chief Inspector's Forty-second Report on Alkali Works, to the Local Government Board.

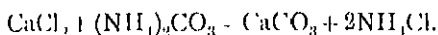
Estimation of Sulphuretted Hydrogen in Liquor -- This estimation is made by boiling a measured volume of the liquor, and absorbing the sulphuretted hydrogen, which is thus driven off, in a solution of either a lead, copper, or cadmium salt, etc. The metal is precipitated as sulphide, and may be then, after filtration and washing, titrated with a standard solution of iodine, or may be oxidised by means of bromine

and precipitated in the form of barium sulphate—compare method for estimation of sulphur in coal and coke.

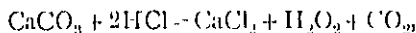
The authors have used an ammoniacal solution of cadmium nitrate, and find the precipitate of sulphide thus obtained very workable, and can be titrated with iodine, in acid solution, or oxidised to sulphate as described, giving accurate results.

The same apparatus may be used as that in which the valuation of ammonia liquor for ammonia is carried out. (See sketch.) 10 c.c. of the liquor are usually sufficient to work upon.

Estimation of Carbon Dioxide.—A portion of the ammonia in ammoniacal liquor exists in the form of carbonate, and this may be estimated by making use of the following reaction :—



That is, by adding a solution of calcium chloride to the liquor, the carbonate of ammonia becomes changed into the insoluble carbonate of lime, which may then be separated by filtration, washed, dried, and ignited to oxide, or titrated with standard hydrochloric acid, when



which denotes that every 100 parts by weight of calcium carbonate will neutralise exactly 73 parts by weight of hydrochloric acid, and consequently, by estimating how much acid is neutralised by titration, the amount of calcium carbonate is determined. Every 100 parts of calcium carbonate are determined. Every 100 parts of calcium carbonate are equivalent to 44 parts of carbon dioxide.

If the carbonate be ignited to oxide of calcium and the latter weighed, every 56 parts by weight represent 44 parts of carbon dioxide.

Both methods give accurate results. The volumetric one is well exemplified in the Chief Inspector's Report on Alkali Works for the year 1905.

Estimation of Hydrocyanic Acid in Liquor—This is done by distilling a measured quantity, 50 c.c. usually, into a solution of caustic soda of semi-normal strength—20 gm. per litre.

ANALYSIS OF AMMONIACAL LIQUOR 33

It is necessary to add a moderate excess of lead nitrate solution before distilling to the liquor in the flask, the object being to retain the sulphuretted hydrogen, in the form of lead sulphide, which would otherwise interfere with the titration of the distillate. The hydrocyanic acid becomes converted into sodium cyanide. It remains now to add to this solution a few crystals of potassium iodide as an indicator, and to run in a measured quantity of standard silver nitrate solution until the liquid becomes just cloudy or opalescent. This indicates that all the cyanide present has become converted into the double cyanide of sodium and silver, and that silver iodide is beginning to form, causing the opalescence. Each cubic centimetric of decinormal silver nitrate used represents '0054 gm. hydrocyanic acid.

Typical examples of tests of ammoniacal liquor for carbonic acid, hydrocyanic acid, ferrocyanide and thiocyanate, sulphide, thiosulphate and sulphite, sulphate, total sulphur and chloride are given in the Report of the Chief Inspector on Alkali Works to the Local Government Board for 1905. In this and other Reports to the Local Government Board will be found the results of a very considerable amount of time and care, which have been expended by the late Mr R. Forbes Carpenter and Mr Linder, in investigating and developing the best and most reliable methods for the analysis of ammoniacal liquors.

CHAPTER V

WORKING UP OF AMMONIACAL LIQUOR

THE ammoniacal liquor, after a primary separation of tar, is pumped to storage tanks, which should be of sufficient capacity to allow time for the efficient settling out of small quantities of tar mechanically carried forward. The presence of tar interferes considerably with the working up of liquor, and every precaution should be taken to ensure efficient final separation. Thus, drain traps should be fitted to the bottom of each storage tank, the liquor outlet being situated some distance higher. Any tar collecting should be run off periodically until liquor appears at the drain tap.

The coke oven liquor is worked up into sulphate of ammonia or into a concentrated liquor of varying strength and degree of purity. In either case the weak liquor is decomposed in a still by steam and lime, the ammonia being thereby liberated along with carbon dioxide, sulphuretted hydrogen, hydrocyanic acid, and excess of steam.

The principle of sulphate of ammonia manufacture is shown in diagram form in Fig. 22. The liquor from the storage tank A on its way to the still receives a preliminary heating in the vessel B, the heating agent being the hot waste gases and steam from the saturator G. The liquor enters the top of the still C at a temperature of about 80° to 85° C., and flows downwards over a series of superimposed trays in a zigzag fashion, meeting an ascending current of steam. Efficient contact between steam and liquor is brought about by various baffling devices in each tray. Milk of lime is pumped into the still by the pump F, and thus serves to expel the "fixed" ammonia. After its lengthened passage through the still the liquor is deprived of its ammonia, and along with the excess of lime and condensed steam leaves the still as "spent liquor" by means of the seal pipe D. The gases and vapours leaving the still C are made to bubble through a bath

of sulphuric acid in the saturator G. Ammonia is absorbed by the sulphuric acid, the strong affinity of these bodies for each other causing an energetic reaction and an increased temperature. The excess steam thus passes through uncondensed, along with carbon dioxide, sulphuretted hydrogen, hydrocyanic acid, etc. A portion of the heat in this mixture of gases and vapours is transferred to the incoming liquor in the heater B, the remainder of the heat being abstracted in a water cooler M. Thus all the steam is condensed, leaving the dried gases to be dealt with in a purifier J to remove all

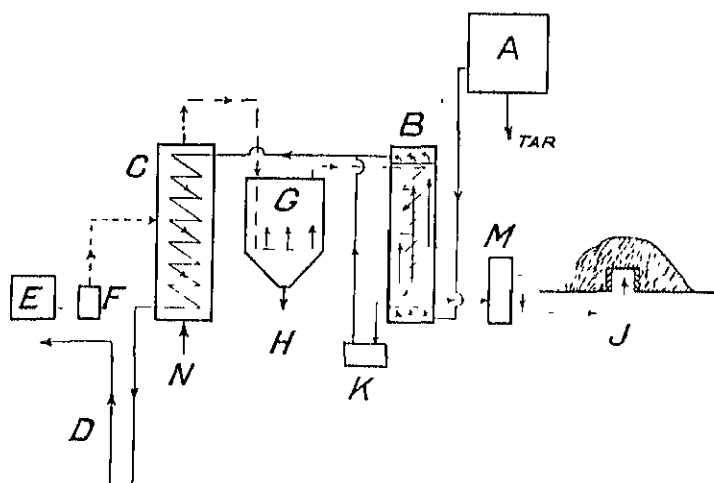


FIG. 22. - General Diagram of Sulphate Plant.

deleterious gases. The steam condensing in the heater B and final cooler M dissolves a portion of the sulphur and cyanogen compounds, and is collected in the form of "devil liquor," which may be returned to the still by means of the pump K.

The heater B is usually of the multitubular type, the liquor passing through the tubes whilst the hot spent gases circulate round the outside. Many types of stills are in existence. In some of these the lime is introduced into an enlarged section of the still itself, in others the liming is carried out in a separate vessel.

A good example of a modern type of still is shown in

Fig. 23 (Chemical Engineering Co.). The main still consists of a series of superimposed sections A, each section having a steam distributing passage B, an overflow weir C, and a sealing plate D. The positions of C and D alternate in such a manner that the liquor descends in a zigzag fashion, passing

in a horizontal direction across each tray in turn. Steam is distributed by the hood E, with serrated edges as shown. It is highly important that the passages B, the serrations of the hoods, and the overflows C be kept clear, otherwise steam will ascend by way of the liquor overflows, or liquor will descend by way of the steam passages. In either case there is a diminution in the efficiency of the still, and serious risk of the liquor being carried forward bodily by the steam giving rise to a priming of the still. Accordingly, provision is made for easy access to these vulnerable points. The hood may be readily removed for cleaning through the opening F, whilst the

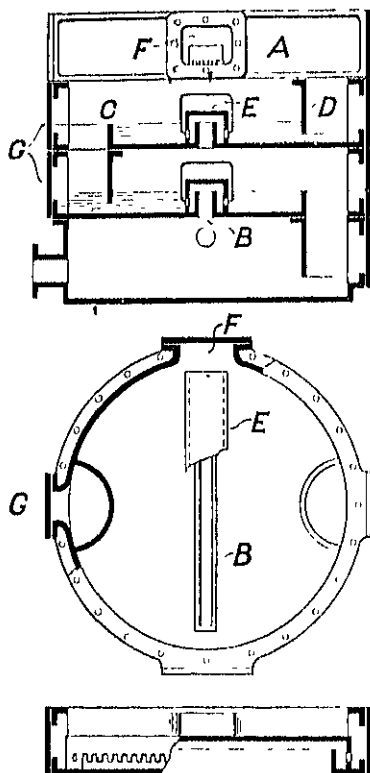
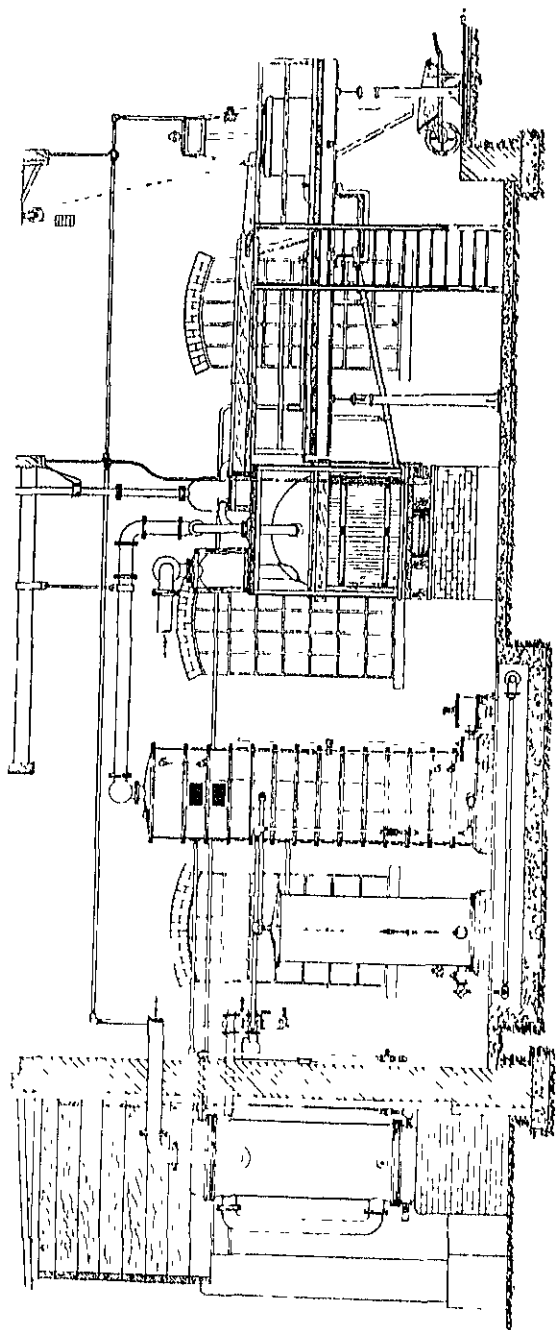


FIG. 23.—Ammonia Still (Chemical Engineering Co.)

overflow passages are of ample dimensions and easily accessible by removing the cover plates G. An arrangement for the introduction of lime is shown in Fig. 24. In this case the liquor, on reaching the fourth tray from the top, passes to the bottom of an external lining chamber shown to the left of the main still. Here it is mixed with milk of lime, the two liquids being thoroughly agitated and brought into



ELEVATION

FIG 24 — S. PLANT — OF AMMONIA PLANT. (Chemical Engineering Co.)

intimate contact by steam from a perforated pipe. The mixture rises to the top, re-enters the still at the fifth chamber, and passes downwards, as already described. The spent liquor may be liberated from the bottom of the still by an automatic float valve or seal pipe so as not to release

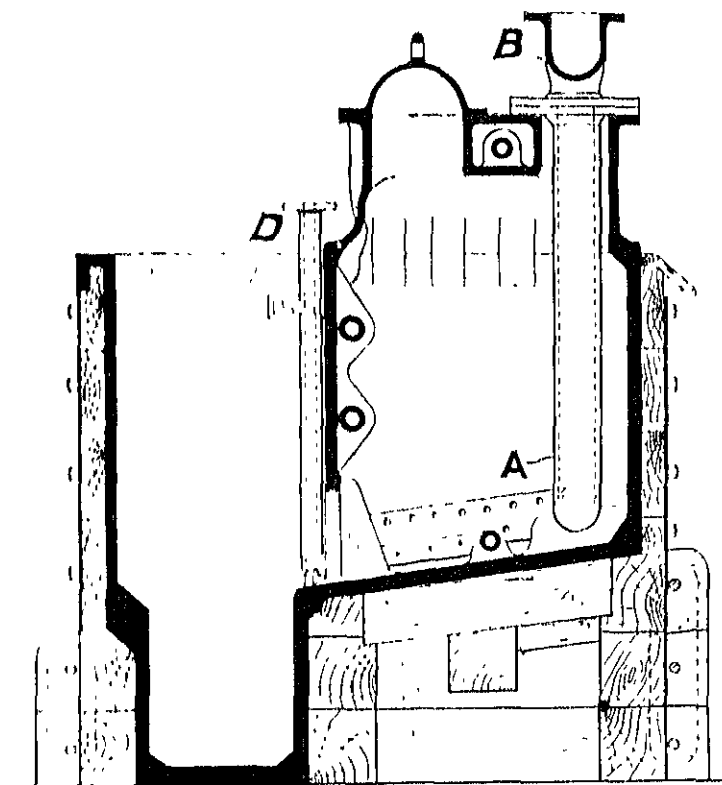


FIG. 25. Saturator. (Joseph Taylor & Co., Bolton.)

the steam pressure. The spent liquor should be carefully examined at regular intervals, and the amount of ammonia passing away estimated. It should not contain more than 0·2 per cent. of ammonia, and with good working is often below 0·1 per cent. The test is conducted on similar line to the total ammonia test in liquors. A bad test may be due to (*a*) shortage of steam, (*b*) shortage of lime, (*c*) blockage in the float valve or seal pot, (*d*) dirty hoods or overflow

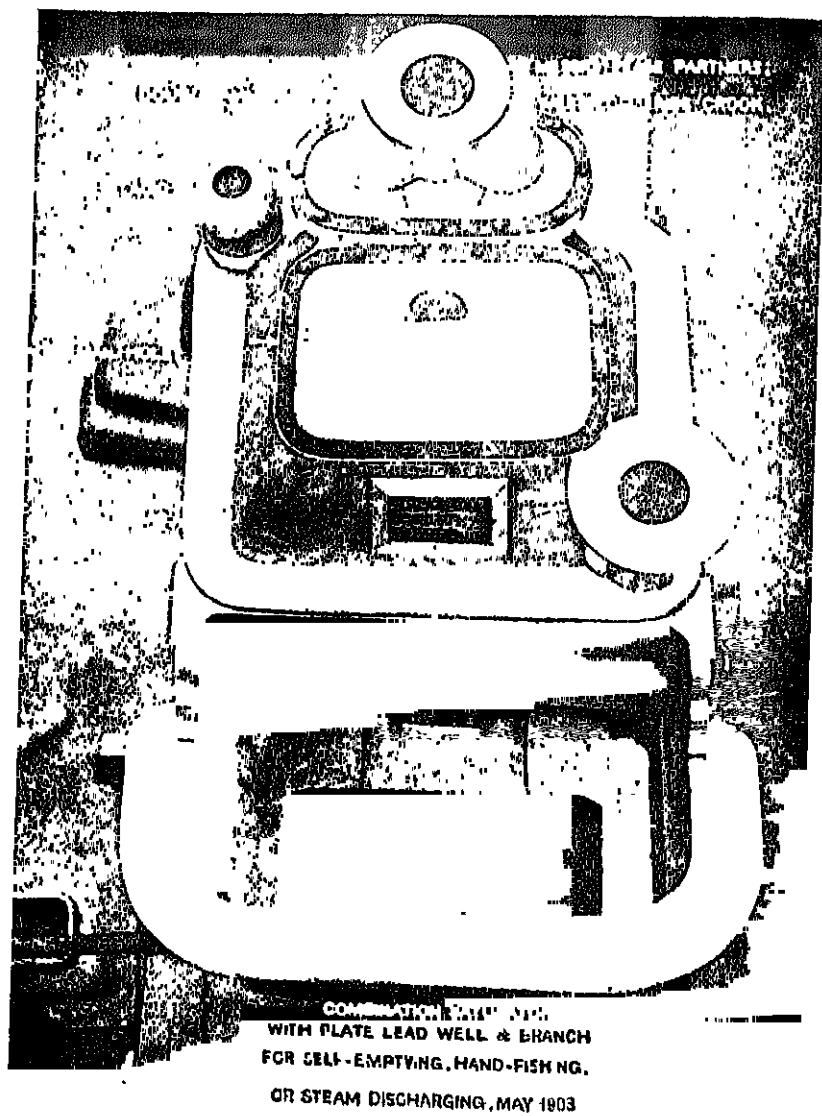


FIG. 25b SATURATOR. (Joseph Taylor & Co.)

The first two may be ascertained by testing the spent liquor for free lime, which ought to be in excess (say up to 5 per cent. free lime). If not in excess the deficit should be made good, and if a re-test shows no improvement the steam supply should be adjusted. If the spent liquor leaves the plant spasmodically, accompanied by large volumes of steam, the condition of the hoods and overflows may be suspected and should be examined, whilst priming would be indicated by a rise in the level of the bath in the saturator or by a sudden lowering of the ammonia test in the case of concentrating plants. A catch box on the outlet pipe to the still is a decided advantage in this respect.

Various types of saturators are in vogue, namely, open bath type, partially enclosed, and totally enclosed types. They may be constructed of strong plate lead supported in a wooden frame, or of thinner lead with a more substantial backing of cast iron. A good example of the open bath type is shown in Fig. 25 (Joseph Taylor & Co., Bolton). The body is made of strong rolled lead plate, the sides being $1\frac{1}{2}$ in. thick, the bottom 2 in., and the top 1 in. The apron plate is stiffened by the insertion of iron bars as shown, whilst the top is supported in a similar manner. These bars are covered with lead well burnt into the body so as not to expose any iron to the action of the sulphuric acid. The vapours are distributed by a perforated blow-pipe A in two portions, either of which, on removal of the breeches pipe B, may be taken out easily for repairs, etc. Acid is admitted at C, whilst a perforated steam-pipe D is introduced so as to blow forward any deposited crystals of sulphate of ammonia into the well E. From thence the sulphate may be fished out by means of perforated copper scoops in the case of small plants, but preferably in the larger plants by means of a sluice valve or steam ejector, the latter being more suitable for continuous working. The waste gases are led away by a branch pipe, fitted in the inspection cover or in one corner of the saturator top. The whole body is supported in a strong wooden framework suitably fitted with steel tie rods, etc., and owing to this and the strong lead plating the saturator is remarkably free from repairs.

The semi-closed type is shown in Fig. 26. The body is

built up of cast iron segments lined with lead, the bottom being in the form of a cone to facilitate removal of the sulphate. The blow pipe B, in the form of a horseshoe, rests on a ledge as shown, the spent gases leaving by the exit C. The condition of the bath may be observed by means of the broad seal pipe D (also of lead), and at the right moment the

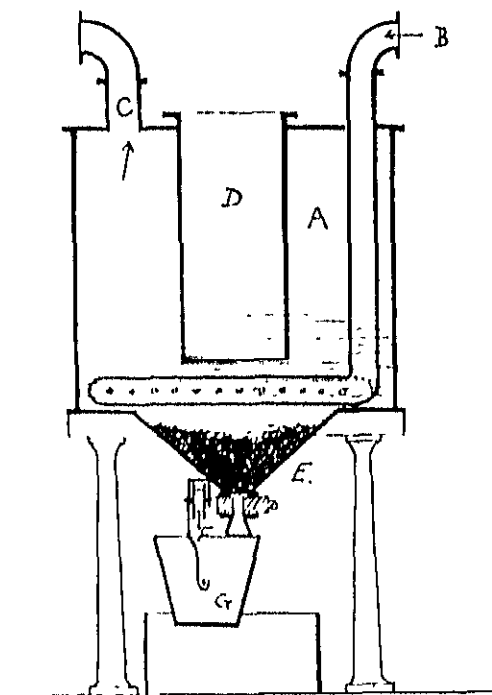


FIG. 26. Self Discharging Saturator.

crystals of sulphate may be discharged through the gun-metal sluice valve at E. The salt may be run out directly on to a draining table or into skips G, which, after suitable drainage, deliver the salt to any portion of the stores by the run-way F.

The enclosed type is shown in Fig. 27 (Chemical Engineering Co.). It is constructed of solid plate lead cased in stout pitch pine lagging, and the principle may be understood from the drawing. The sulphate is removed by an ejector, which

may be of lead or copper, the latter being more conveniently handled. Steam or compressed air is blown in at E, passing down the smaller tube which communicates with a small nozzle fixed centrally in the larger tube and looking upwards. The lower end of the delivery tube is enlarged as shown, and is fitted with openings through which the sulphate is sucked into the delivery tube. An enlargement in the form of a lead box G is fitted to carry off surplus steam or compressed air,

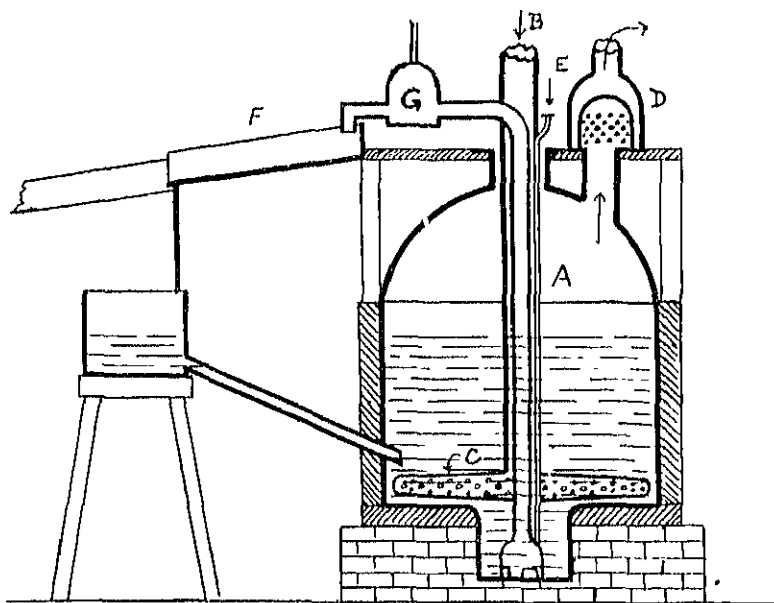


FIG. 27 "Wilton" Saturator.

and to allow the sulphate to flow quietly to the draining table F. Any mother liquor separating from the mass is returned to the saturator. After a preliminary draining the sulphate may be run directly into a centrifugal machine (Fig. 28, Wilton type). This consists of a basket A made of perforated copper plates reinforced with copper rings, and attached to the shaft K. The revolution of the basket forces the liquor by centrifugal action through the finer perforations of a loosely fitting lining to the basket, thence through the coarser perforations of the basket itself into the space en-

closed by a lead outer casing B, from which it passes by the outlet E to the mother liquor well or back to the saturator. After a few minutes' "whizzing" the basket is allowed to come to rest, and the dried sulphate is conducted to the shoot D and elevator F by lifting the valve C (loose on the spindle).

The method of working a saturator has a marked influence on the quality of the sulphate produced. In face of severe

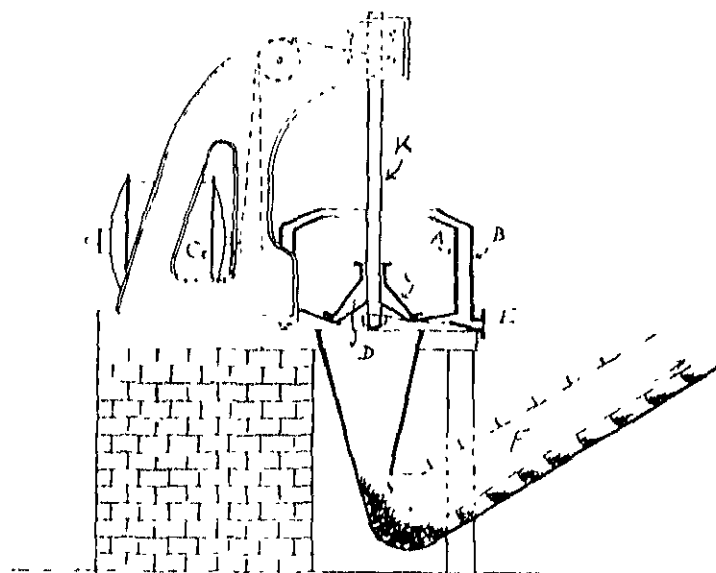


FIG. 28. Centrifugal Drying Machine.

competition from the Continent the quality has received more attention recently, and the Sulphate of Ammonia Association strongly advises its members, as an act of self-interest, to endeavour to manufacture a product containing at least 25 per cent of ammonia, and not more than 3 per cent moisture and 1 per cent free acid. It also suggests that the sulphuric acid used should be as free as possible from iron and arsenic, and should never contain more than 5 per cent ferric oxide or '05 per cent arsenic. With such acid a continuous working of the saturator is possible, but in using an arsenical acid the writer's experience is decidedly in favour of an inter-

mittent process. The gases passing into the saturator contain sulphuretted hydrogen which, reacting on the arsenical compounds, ultimately causes a deposit of strongly yellow arsenious sulphide. In the ordinary course of events this would settle down along with the crystals of sulphate of ammonia, which in consequence becomes discoloured to an objectionable extent. One may remedy this state of affairs by previously precipitating the arsenic in a separate vessel, utilising the sulphuretted hydrogen in the waste gas for this purpose.

One difficulty in this case is due to the fact that at the strengths of acid usually supplied for this purpose, free sulphur is also deposited in a fine state of division, interfering with the filtering process, the precipitation being best carried out with acid of about 110° Tw. and under, whilst additional plant is necessary. Another method is to precipitate the arsenious sulphide in the saturator itself. In this case the bath is made up to 68° Tw., in the first place with sulphuric acid (144° Tw.) and water, in succeeding baths with acid and mother liquor. An energetic reaction immediately follows, the Tw. rising to 69° or 70° Tw., and the temperature rising from 108° C. to 112° C. in the first two hours. At the commencement of the boil, tar, anthracene oil, or creosote oil is poured into the bath to the extent of about half a gallon per ton of sulphate produced. By the aid of these oils the arsenical precipitate held in suspension is coagulated, and rises to the surface with the oily matter in the form of a scum. It is advisable to remove the great bulk of this scum in the early stages of the bath. After an hour or two the specific gravity of the bath and the temperature begin to drop gradually, until on reaching a gravity of about 62° Tw. and a temperature of about 106° C. crystals of sulphate of ammonia become evident. The bath may be allowed to drop to about 60° Tw. when the discharge of the sulphate may be commenced. The discharge should be completed by the time the bath reaches 55° Tw., as below this there is a risk of the bath becoming neutral, with a possibility of the production of blue salt. If the discharge commences too soon, say above 60°, the crystals are in a much finer state of division, and on draining hold the acid tenaciously. This "floury" salt is

also difficult to drain, and is usually associated with a high moisture and free acid test. Under conditions similar to the above the writer has had no difficulty in producing good grey salt of satisfactory analysis from arsenical acid. If de-arsenicated acid is available, after the first bath has reached 60° Tw, a small stream of acid is allowed to enter the saturator, and the contents are brought down gradually to 58°.

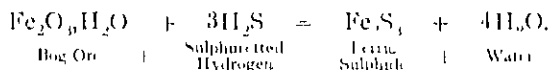
From this point the supply of acid is adjusted (according to the amount and strength of liquor passing through the still, etc.) so as to maintain a gravity between 58° Tw. and 56° Tw. continuously. As a check the free acid in the bath should vary between 1 and 8 per cent. Under these conditions sulphate of ammonia is being continuously produced, and is steadily ejected at the rate of formation, whilst acid is being fed in continuously. These conditions are not difficult to maintain, and result in the production of snow-white sulphate, with large crystals easily drained, and giving, even without the use of a centrifugal drying machine, a salt quite up to the standard recommended by the Sulphate of Ammonia Association.

Blue sulphate may be produced in various ways. A common cause is the neutralisation of the bath, which is liable to occur if the bath is allowed to approach a gravity of 51. It is probable that in this case the iron salts in the acid are precipitated, and combining with cyanogen compounds become fixed as ferrocyanides. On the admission of further acid, the ferrocyanide is converted to ferrous-ferrocyanide by the sulphate of iron. This ferrous salt on exposure to the atmosphere is oxidised to Turnbull's blue or Prussian blue. Thus the blue colour is not always apparent in freshly ejected sulphate, but develops in a few days. However, the smell of a neutral bath is typical of the conditions, and if a dark grey salt appears at the same time, it should be treated with suspicion, and placed in the stores apart from any other sulphate. Alkalinity may also be brought about by a priming of the still, which at the same time reduces the temperature of the bath, a lower temperature favouring the fixation of cyanogen compounds. A damaged blow-pipe may also lead to blue salt. Thus if the holes become enlarged, or a split in the pipe occurs, the contact is concentrated into a small

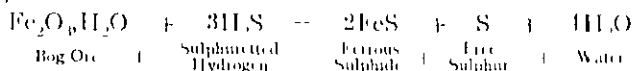
area in which local alkalinity is developed. In this case, in addition to the risk of discoloration, there is a probability of loss of ammonia, owing to inefficient spreading of the vapours. In many cases, as a safeguard, a baffle box is fitted to the outlet pipe. In this the waste gases are brought into contact with the acid entering the still, and a portion, if not all, of the escaping ammonia is returned to the saturator. The waste gas leaving the saturator after condensation of excess steam consists of a mixture of gases which would form a source of danger in the atmosphere, and must be treated for the removal of some of these. A typical analysis of waste gas is given below:—

Sulphuretted hydrogen	-	-	2.0	per cent. by volume.
Hydrocyanic acid	-	-	2.0	" "
Carbon dioxide	-	-	82.0	" "
Nitrogen	-	-	14.0	" "

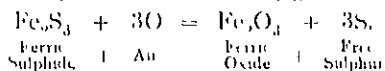
Sulphuretted hydrogen gas may be dealt with in several ways. At some works it is burnt, and the sulphur dioxide thus produced used for the manufacture of vitriol. At others, the gases are passed through purifiers containing layers of bog ore or oxide of iron, alone or mixed with sawdust, which takes up the sulphur and some of the cyanide. The sulphuretted hydrogen in passing through this material is decomposed, its sulphur being taken up by the iron oxide forming sulphide, thus:—



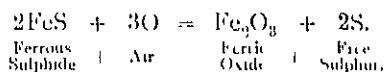
Also,



When the bog ore becomes highly charged with sulphide it is exposed to the action of the atmosphere to "revivify" it. This comes about by the action of oxygen, thus:—



Also,



This revived material, consisting of ferric oxide and free

sulphur, is used over and over again in the purifiers until it becomes charged with 60 to 70 per cent. of sulphur, when it is disposed of generally to vitriol manufacturers for the production of sulphuric acid.

In some cases the sulphur is recovered in a solid form in a Claus kiln.

The plant is simple to operate, and with reasonable care gives good results. The principle is shown diagrammatically in Fig. 29.

The waste gases pass first through a coke tower A to remove any excess of moisture, thence into the Claus kiln proper B. This kiln is filled to a depth of about 3 ft. with lumps of iron ore, the bottom layers being in good-sized lumps 3 or 4 in. in diameter, the middle layer rather less,

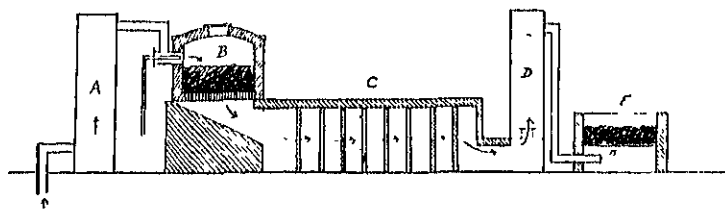
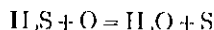


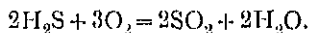
FIG. 29.—Claus Plant for Sulphur Recovery from Waste Gases.

and the top layer of still finer lumps, finished off with a coating of bog iron ore such as is used in the purifiers. The whole is supported on iron grids so as to allow a free passage of the mixed gases through the mass. The principle upon which the reaction in the kiln is based, is that when sulphuretted hydrogen is mixed with a certain volume of air—usually about 10 per cent. is required—and heated to a certain temperature, the following reaction goes on :—



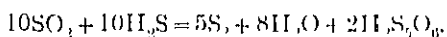
The initial heat requisite to start the above reaction is supplied by a few shovels full of hot coal or coke put in through the top of the kiln, and, once started, the heat is easily maintained by the catalytic action between the oxide of iron and the mixture of sulphuretted hydrogen and air. The heat is continuous if the proper relative proportion of these gases is regulated, and this is not at all difficult. If too

much air is going in there will be indications of sulphur dioxide which can be recognised by its action on litmus paper. Naturally this means loss of sulphur, as well as the cooling action on the kiln.



Again, if the air supply is deficient, a portion of the sulphuretted hydrogen passes through the oxide without decomposition, and may be detected by means of paper soaked in a solution of lead acetate. The slightest trace of sulphuretted hydrogen turns this to a brownish-black colour at once, owing to the formation of lead sulphide. The gases may be conveniently tested at two points—one near the kiln, the other near the base of the limestone tower D, through suitable holes left in the brickwork, fitted with wooden stoppers.

When the kiln is working satisfactorily and the reactions going on properly, it is generally found that there are indications of both sulphuretted hydrogen and sulphur dioxide. These gases react in presence of each other thus:—



The sulphur thus set free is in an extremely fine state of division, and the milky effluent from the limestone tower is due to this finely divided sulphur in suspension, and which has most probably been produced by practically the same reaction as above, *i.e.*, by the interaction of sulphuretted hydrogen with either gaseous sulphur dioxide or a solution of the sulphite.

The reaction is also interesting because it most probably represents that which takes place in nature on a large scale, resulting in the deposits of native sulphur usually found in volcanic districts. Both sulphuretted hydrogen and sulphur dioxide are present in volcanic gases. After reaction and deposition of sulphur the remaining gases pass on and upwards through a tower D, which is loosely packed with lumps of limestone, over which a trickle of water is fed from a spray at the top of the tower. This is to neutralise any acidity due to any sulphur dioxide which may remain in the gas. From the tower D the gases are led through purifiers E to remove remaining traces of sulphuretted hydrogen and cyanides.

ANALYTICAL PRACTICE

The sulphur in the chamber next to the
the dry and runs down in the
the chamber on in this state or
the chamber on to a deep and weigh-
the sulphur in the later
the sulphur is beautifully crystalline
the sulphur is also in a very
the sulphur is in an amount of moisture,
the sulphur containing 90 to 95
the sulphur containing moisture, with a trace
the sulphur, probably produced by
the sulphur by acid makers in the
the sulphur in addition to those re-
the sulphur there are others

The sulphur is produced by the interaction of
the sulphur and hydrogen leads to the pro-
the sulphates are also formed
the sulphites.
The sulphur has made most
the sulphur in regard to the reactions
The result of their investiga-
the sulphur presented before the Society of
the sulphur in 1901 and June 1901, and they
the sulphur of that Society.
the sulphur reacts with steam,

ANALYTICAL PRACTICE

The sulphur is a mixture of hydro-
the sulphur is produced through highly
the sulphur that the percentage was
the sulphur was 100 percent. This
the sulphur in the recovered
the sulphur due to ammonia having
the sulphur plant, therefore, not only
the sulphur of purifying the exit
the sulphur dangerous hydro-
the sulphur and the characteristic
the sulphur when the kiln is cleared

out. When necessary to close down the plant for cleaning it is most necessary to allow ample time for the gases in the chambers to diffuse out, by opening the brickwork about two days before the workmen are allowed to enter; even then every precaution must be taken, as the gaseous mixture hangs about the walls very tenaciously, and is most deadly. A good quality of recovered sulphur should have an approximate analysis as follows:—

Moisture	-	-	-	3 to 5 per cent.
Ammonia, calculated as carbonate				3 to 4 „
Mineral matter, non-volatile	-			1 „
Sulphur	-	-	-	90 to 93 „

The second-grade quality contains more moisture and ammonium salt. The ammonia may be determined indirectly by estimating the loss on washing the sulphur with water, or more accurately by distillation with sodium hydate into normal sulphuric acid. The sulphur may be taken by difference after careful estimation of all impurities. It may also be extracted by carbon disulphide, in which case any amorphous sulphur will be unacted upon. The mineral matter, other than sulphur, is that which remains after burning away the sulphur as completely as possible.

The Testing and Valuation of Ammonium Sulphate.—

This by-product, if reasonably pure, is white in colour. In some instances, owing to various defects in the methods of its recovery, the salt is blue, and more rarely brown. In the majority of cases, especially with blue salt, the value is much depreciated on account of colour, but in a few instances, generally with Chinese traders, a brown to black salt is insisted upon, and consequently to meet this requirement a white salt is mixed off with some dark colouring matter to give the desired effect. This, of course, lowers the percentage of ammonia.

Sulphate of ammonia, when absolutely pure and dry, contains 25.75 per cent of ammonia (NH_3). The by-product from coke manufacture, if well made, ought to contain 24.5 to 25 per cent. The salt as usually produced contains also a certain amount of moisture, which varies from about 5 to 2.0 per cent. In addition to this, there is always more or

less "free acid" in the salt. This ought not to exceed .5 or .6 per cent. If the amount is much more than this it is most likely to cause trouble when the material is loaded up in sacks for transport, owing to the action of the acid on the sackcloth, which eventually causes the bottom of the sack to give way entirely. This is the more likely if at the same time the salt is abnormally wet. The terms of contract for a supply of this material usually stipulate that there shall be a minimum of 24 per cent. of ammonia, and that the salt shall be free from cyanide, by which is meant the ferrocyanide which causes the blue colour.

The estimation of ammonia in sulphate may be made in the same apparatus as that in which the liquor is tested, and the principle of the test is the same, namely, that the sulphate, of which a weighed portion is taken, is decomposed by the addition of sodium hydrate, its ammonia liberated in the free condition as NH_3 , which is passed into a measured quantity of a normal or standard solution of sulphuric acid. From the amount of acid neutralised a measure of the ammonia is obtained, each cubic centimetre of normal sulphuric acid neutralised representing .017 gm. of ammonia (NH_3).

An example of an actual test is as follows: 5 gm. of the sulphate were dissolved in water and diluted to 500 c.c. in a flask. After thoroughly mixing, 25 c.c. were taken out by means of a pipette, and transferred to the distillation flask. This portion therefore contained .25 gm. of the salt. A moderate excess of sodium hydrate being added, the distillation was gradually carried on for about three-quarters of an hour into the bulbed tube containing 10 c.c. normal sulphuric acid. When all the ammonia was over, the U tube was detached, and its contents rinsed into a porcelain basin and titrated with a normal solution of soda, 6.35 c.c. being required to neutralise the remaining acid. Hence the acid neutralised by the ammonia liberated from .25 gm. of the salt $= 10.0 - 6.35 = 3.65$ c.c., and $3.65 \times .017 = .062$ gm. NH_3 .

That is, .25 gm. contains .062 gm.

1.00 " " .248, or 100 contain 24.8 gm.

That is, 24.8 per cent. ammonia in the salt.

The amount of moisture in sulphate may be determined

by weighing off 5 or 10 gm., and drying in a water bath at a temperature of 100° C. for about two hours until the weight becomes constant. The loss represents moisture.

The free acid present is determined by dissolving 5 gm. of the salt in distilled water, adding a few drops of methyl orange solution, and titrating with standard soda. If great accuracy is necessary, it is advisable to use decinormal soda, that is, one-tenth the strength of the normal, or .001 gm. hydrate per 1 c.c.

The sulphuric acid used in the production of sulphate of ammonia should be practically free from impurities, especially iron, arsenic, and total solid residue, principally lead sulphate. The amount of total solids can be readily ascertained by evaporating a measured quantity in a weighed platinum dish—this should be done in a good draught cupboard—and finally heating up to dull redness in a gas muffle, or over a good Bunsen flame. If the amount of solid residue is excessive, the quality of the sulphate suffers.

The iron may also be conveniently estimated in this residue by digesting it with concentrated hydrochloric acid until all the iron oxide is dissolved, then either determining volumetrically by means of $\frac{N}{10}$ potassium dichromate or permanganate, or by filtering off any insoluble matter, separating any lead by means of sulphuretted hydrogen, then precipitating the iron in the filtrate, after oxidation with a little nitric acid, by means of ammonium hydrate, boiling, filtering, washing, and finally, after ignition, weighing as ferric oxide. The volumetric method is much simpler and quite accurate. If the amount of iron is excessive it increases the likelihood of the formation of blue salt (see p. 41).

The arsenic content is ascertained as follows. 10 to 30 c.c. of the acid, or preferably an equivalent weight, are taken according to the amount of arsenic suspected, and diluted with about four times its volume of distilled water. About 10 c.c. of sulphurous acid are added, and the whole boiled until the smell of SO_2 has disappeared, to reduce any arsenic in a higher state of oxidation to the lower arsenious condition. The solution is cooled and thoroughly saturated with sulphuretted hydrogen gas. The arsenic is thus precipitated

as arsenious sulphide, As_2S_3 , and should be left to settle, preferably over night. Filter through a tared filter and wash with hot water containing a little H_2S until the washings are free from sulphuric acid. Transfer the paper and contents to the water bath, and dry at 100°C . until the weight becomes constant. The arsenic sulphide should now be treated with carbon disulphide to remove any free sulphur. The residue should be again dried in a water bath until a constant weight is obtained. As_2S_3 contains 60.93 per cent. of arsenic, and from this we may calculate the percentage of arsenic in the weight of acid dealt with.

An average amount of the above impurities in the de-arsenicated sulphuric acid used is as follows:—

Total solids	-	-	-	·05 to ·07 per cent.
Ferric oxide	-	-	-	·015 to ·035 „
Arsenic	-	-	-	<i>nil</i> to traces.

Manufacture of Concentrated Liquor.—This method of working up the ammoniacal liquor on coke works is now being extensively adopted, and in many respects possesses advantages over the sulphate method. No acid is required, and as no waste gases are given off, the expense of purification is dispensed with. The plant as a rule requires very little attention, takes up comparatively little room, and less labour is required in the working of it. The principle is very simple, consisting of:—

- (a) Distillation of the coke works liquor, as in sulphate manufacture.
- (b) Dephlegmation of the vapours to return the bulk of the excess steam back to the still.
- (c) Condensation of the comparatively dry ammonia vapour, the result being a concentrated solution, the strength depending largely on the efficiency of the dephlegmation.
- (d) Absorption of any ammonia escaping from (c) in washers, scrubbers, etc.

An efficient type, as manufactured by Messrs Brunner, Mond, & Co., is shown in Fig. 30. It consists of a series of absorbing and condensing vessels, A, B, C, D, E, and a cooling vessel F. These absorbing vessels are constructed

of cast iron, the vapours being admitted by a dip-pipe with an efficient spreading device to bring about a thorough contact between the gases and liquids. The temperature

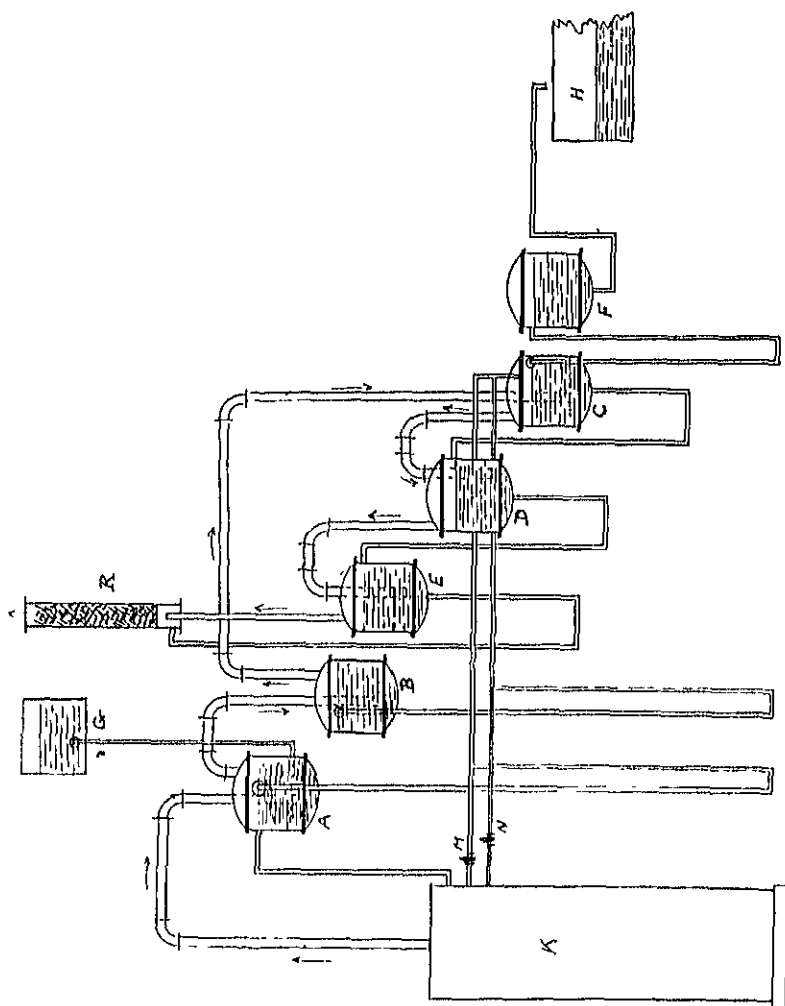


FIG. 39.—Concentrated Liquor Plant.

of each vessel is regulated by the flow of cold water through enclosed cooling coils of lead piping. The vessel A may be looked upon as a dephlegmator, B as a main condenser, C, D, E as absorbers, forming along with the coke tower R

an effective counter-current scrubbing system. The vapours from the still pass through the absorbing vessels in the above order, each vessel containing about 2 ft. of liquid. The total depth of liquid through which the vapours are forced is about 10 ft., as opposed to about 2 ft. of acid in sulphate making. The pressure on the top of the still is thus higher in the case of concentrated liquor, and provision for this must be made in designing the still. In the plant described the gases from the still pass into the first absorbing vessel A. Here they are cooled by coils, through which cold water or (as shown in the drawing) cold weak liquor is run. Thus the first vessel may be used as a superheater. As the bulk of the condensation takes place in this vessel, a great proportion of steam is condensed, and the liquor from this vessel is usually run back into the still through the cock M. The temperature in this vessel is too high for complete absorption of ammonia, and the gases pass on through the other absorbing vessels, B, C, D, E, in the order named. The temperature in these vessels is controlled by cooling coils (not shown in sketch), and the whole of the ammonia is absorbed. The gases, if any, from the final absorbing vessel E pass through a coke tower R, down which a small stream of cold water runs. This water takes up the last traces of ammonia or sulphuretted hydrogen, and passes on through D to C, taking up more ammonia in its passage. It will be seen that the liquor from B also flows to C. Thus the liquor in C is the final liquor, but to avoid loss by volatilisation, the liquor is cooled in vessel F before passing to the store tank H.

Besides ammonia, carbon dioxide and sulphuretted hydrogen and hydrocyanic acid are absorbed in the various vessels, and the final concentrated liquor is really a mixture of ammonium carbonate, ammonium sulphide, ammonium hydrate, ammonium cyanide, etc.

The total ammonia in the liquor by the above plant may be brought up to 17 per cent., but it is not advisable to go beyond this point, as the tendency to crystallise increases rapidly, and there is danger of stoppages in the pipes, chiefly through ammonium carbonate. In satisfactory working the pressures on each vessel should show a gradual decrease to atmospheric pressure, and the temperatures on the vessels

should also decrease uniformly. The following figures show an average working :—

Pressures :—

Top of still.	A.	B.	C.	D.	E.
12	9½ to 10	7½ to 8	5 to 6	3 to 3½	0 to 1 in. mercury.

Temperatures :—

Top of still.	A.	B.	C.	D.	E.
100° C.	80° to 85°	70° to 75°	50° to 55°	40°	25°.

Per cent. of ammonia :—

A.	B.	C.	D.	E.
10 per cent.	15 per cent.	17 per cent.	13 per cent.	4 per cent. NH_3 .

A typical analysis of a concentrated liquor is given below :—

Ammonium carbonate	-	-	35·0 per cent.
„ sulphide	-	-	5·0 „
„ hydrate	-	-	4·0 „
„ cyanide	-	-	·1 „
Ammonia, as NH_3	-	-	17·0 „

A preponderance of ammonium carbonate will be noticed. If the weak liquor from the coke plant contains excessive proportions of carbon dioxide, ammonium carbonate is deposited in the coolers and piping in a troublesome manner if the degree of concentration exceeds about 15 per cent. of ammonia. In some cases a portion of this carbon dioxide is removed separately, allowing a higher degree of concentration, say up to 25 per cent., whilst in rarer instances the whole of the carbon dioxide as well as sulphuretted hydrogen is removed, the production of fairly pure aqueous ammonia being then aimed at. A great proportion of the carbon dioxide, as well as appreciable quantities of sulphuretted hydrogen, may be removed by means of a preliminary heating of the weak liquor. Thus at a temperature of about 95° C. we can drive off these objectionable gases along with only slight proportions of the ammonia. The foul gases evolved may be led into the foul gas main, or may be passed through an acid seal to retain ammonia, the remaining gases being led off by a vent pipe. The hot, partially purified liquor may then be treated in an ammonia still in the manner already described. Another

method of removing carbon dioxide is to pass the gases after dephlegmation through a washer fed by a continuous stream of milk of lime, which may then be admitted to the still in the usual manner. If the purest product is sought, excess of lime is necessary, and two or three washers are used. Permanganate of soda or ferrous sulphate may be used to remove the last trace of H_2S . Tarry matters, pyridine, etc., are removed in a heavy oil washer. After passing through a final charcoal filter or coke scrubber the purified ammonia gas is absorbed in distilled water, giving a water-white aqueous ammonia.

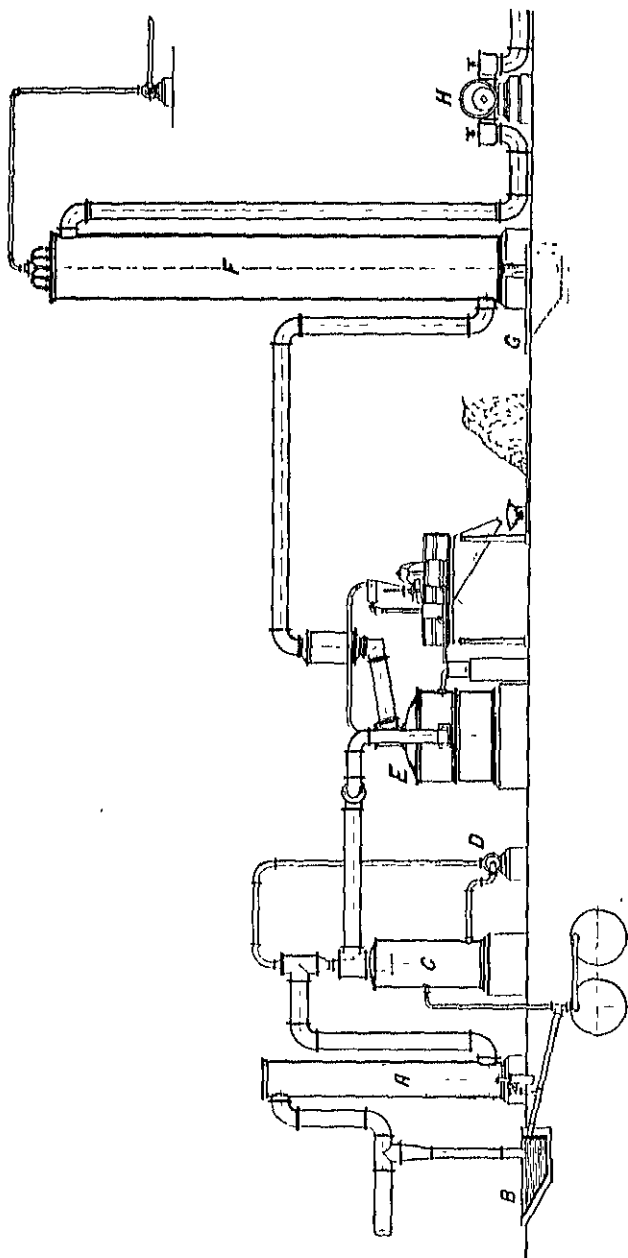
CHAPTER VI

"DIRECT" PROCESSES OF AMMONIA RECOVERY

UNTIL recently ammonia was almost entirely recovered at coke plants by a water absorption system as described in previous chapters. This process is attended by certain disadvantages. A low temperature of the gas is necessary for efficient recovery; varying quantities of water are introduced into the scrubber, increasing the bulk of liquor which with washed coals is, apart from this addition, a serious item; manipulation of the liquor from various points leads to losses from evaporation, etc.; whilst the increased bulk of liquor necessitates a heavy steam consumption in the stills, and an excessive quantity of spent liquor. In some cases an acid washer or scrubber is substituted for the usual water-fed type, the solution of ammonium sulphate being evaporated to the crystallising point or used up in the saturator, but these processes do not appear to have made headway in coking practice. In considering ammonia alone the thermal losses in (*a*) cooling the gases and (*b*) distilling the liquor represents the reverse of economy, and to minimise these losses, Brunk in 1903 attempted to recover ammonia in a "direct" system by passing the hot gases through sulphuric acid. The process at the time failed through the inefficient removal of tar from the hot gas, giving rise to dirty sulphate, but since then effective tar extracting systems have been developed and the drawback of discoloured sulphate has been removed. Efficient tar extraction is a prime essential, and is brought about by frictional methods, such as (*a*) intimate contact with a spray of tar, creosote, or liquor, (*b*) centrifugal methods, (*c*) bubbling through hot tar, etc. Another essential is the prevention of condensation of the water vapour before leaving the saturator. For this purpose the gas, up to its entry into the saturator, must be kept at a temperature above the dew

point at any particular plant. This dew point varies with the moisture contents of the coal and the proportions of water vapour and fixed gases in the mixture entering the saturator. With washed coals the figure is usually in the region of 80°C ., whilst with dry coals it approaches 70°C . There is thus a decided gain in thermal efficiency in cooling the gases to, say, 80°C . instead of 25°C . However, as it appears probable that benzol recovery will be an essential part of a modern by-product plant in future, we must consider the ammonia question in conjunction with benzol. Thus in benzol recovery we must cool the gas to 25°C . whatever process of ammonia recovery is used, and if we are to reduce the temperature of the gas to this extent after the saturator the gain in thermal efficiency disappears.

There is an advantage in cooling *after* the abstraction of ammonia, as the condensates are then practically free from ammonia and constitute an effluent free from lime, requiring no settling pools, and of considerably less volume than obtains in the older indirect processes. Other direct processes recover the tar as in the older systems, by gradual cooling followed by some form of tar extractor (usually of the impact type). Under these conditions the water vapour is also condensed, and the liquor produced, though lessened to the extent of the amount of water formerly added in the scrubber, must be treated with lime and steam in the usual manner. Ammonia is expelled in the free condition and is admitted to the main gas supply, which then passes through a saturator. This type of plant may be more correctly termed a semi-direct process, since an appreciable amount of liquor is made requiring lime and steam, and a separate still, whilst in the true direct processes only inappreciable quantities of liquor are produced, owing to the higher temperature in the initial stages. Though naphthalene troubles are not unknown in indirect and semi-direct processes, the gradual cooling removes some naphthalene by way of the tar, and the trouble is not as acute as sometimes experienced in direct plants. In many cases the latter adopt special means for removal of naphthalene after the saturator and prior to the benzol scrubbing system. Both direct and semi-direct systems offer advantages as compared with the older indirect method, but as to the relative merits



F.G. 31.—OTTO DIRECT RECOVERY PLANT.

of direct and semi-direct plants, definite advantages peculiar to one system are counterbalanced by equally definite disadvantages, and so far the writer, from observations at several plants of both types, is unable to express any preference for either type. The various modifications of these processes are described *separately* :—

The Otto process (Fig. 31) removes the tar by means of a specially designed spray extractor after a preliminary regulation of the gas temperature by means of an air cooler A. The heaviest tar is condensed in the gas main and is removed by means of the tar catch tank B designed for easy removal of pitch deposits, etc. The essential part of the system is the extractor C consisting of a vertical pipe 6 to 8 ft. long, slightly conical, the dimensions being determined by the nature of the liquid used for spraying. On the Continent tar is usually used, but liquor has been used in this country to good effect.¹

The liquor or tar is circulated by the centrifugal pump D and collects in the tank below the spray, the excess overflowing to the store tank. Any chloride of ammonia present is scrubbed out along with the tar and dissolves in the liquor. Mr Purves states that ammonium chloride is not so effectively removed when tar alone is used. He points out that the extraction of the tar is purely frictional, and the temperature of the liquor is too high for free ammonia to be dissolved, whilst it is evident that if the temperature of the gas and liquor is kept just at the dew point, neither deposition nor evaporation of liquor will occur. He further states that the separation of heavy tar is complete between 70° C. and 80° C., his tests of the tar showing at the same time that only inappreciable quantities of light oil are absorbed, the latter passing through the saturator E. The proportion of ammonium chloride entering the saturator is very small under these conditions, whilst the writer's tests on salt, made with tar as a spraying medium, indicate that the chloride is only partially decomposed and is deposited with the sulphate.

¹ "The Application of Coke-Oven Carbonizing and Otto Direct Ammonia Recovery to Gas Works' Requirements," G. T. Purves, A.M.I.C.E., Inst. of Gas Eng., June 1911.

After passing the saturators the ammonia-free gas is treated in a specially designed naphthalene scrubber F by a series of powerful water jets. The water descends and carries down with it some of the naphthalene, which may then be recovered from the catch tank G. The gas now enters the exhauster H, which forces it forward through a cooling system and a benzol scrubbing system, and thence back to the ovens. The saturator for this and other direct processes is designed on a much larger scale than the ordinary type, since in addition to the ammonia evolved the whole of the gas from the coke ovens must pass through this apparatus.

The Simon-Carves direct process (Fig. 32) aims at the

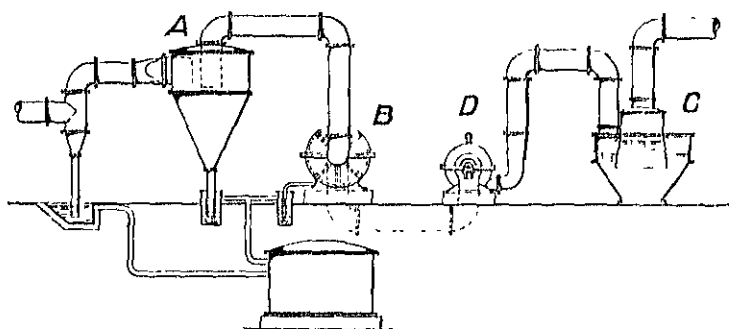


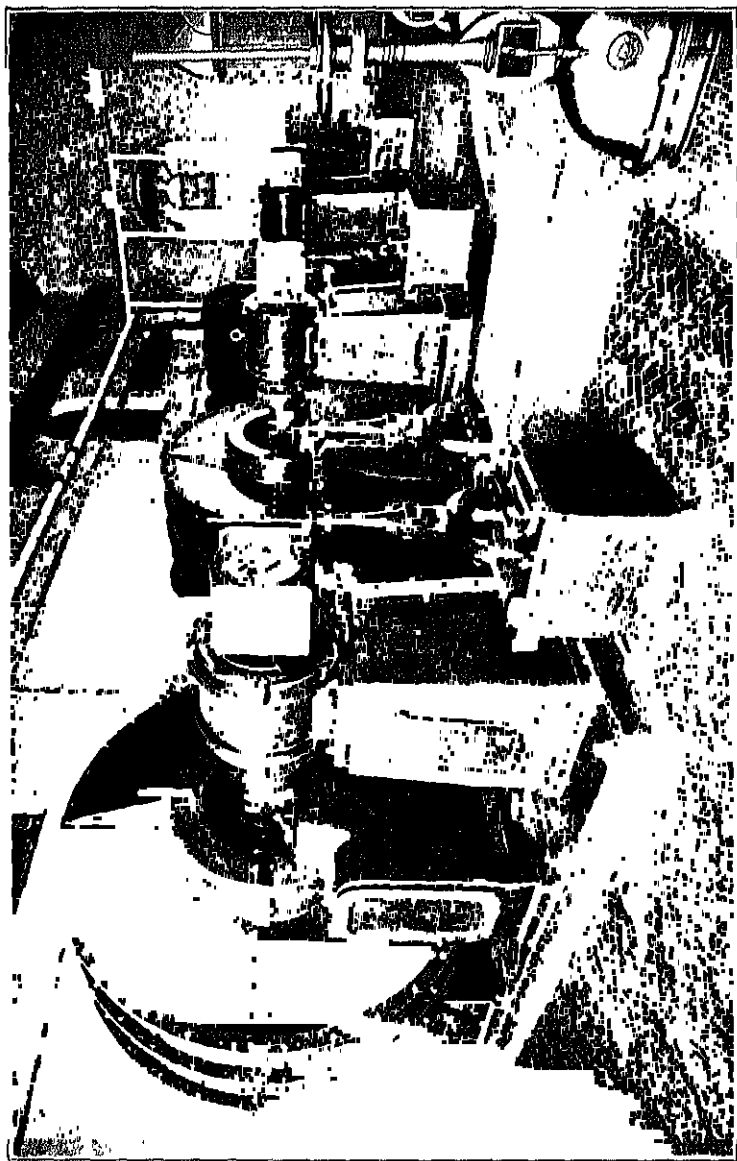
FIG. 32.—Simon Carves Direct Recovery Process

removal of the tar in a hot condition in two stages, both of which are dependent on the centrifugal action on constituents of varying specific gravity. Owing to the great difference in specific gravity of the heavier tar and gas, it has been found that a centrifugal separator of the cyclone type without any moving parts is suitable for the first stage dealing with the heavier tars. The gas enters the cylindrical portion of the cyclone separator A, through a tangential inlet, the action of the exhauster imparting a rotary motion to the gas. This is maintained by reason of the conical shape of the lower portion counteracting the gradually diminishing velocity of the gas, which leaves the apparatus through a central outlet pipe extending some distance below the cover to prevent any interference with the cyclonic action. The drops of tar are thrown outwards towards the periphery of the separator,

where they coagulate and are collected through a seal pot. To remove the lighter tars a more energetic action is required, and this is obtained in the dynamic tar extractor *u*, in which a very rapid rotary motion is produced by vanes revolving at a high speed. The finer drops of tar still in suspension after the cyclone are brought into violent contact with one another, combine into larger drops, which collect in the lower portion of the casing and are drained off. In the case of coals containing high proportions of chlorides, a little water is allowed to condense in the dynamic separator. This water dissolves out the greater portion of ammonium chloride, forming a solution which may be worked up to a marketable solid product. This appears to be the most feasible method of dealing with this constituent, as the ammonia is already fixed as chloride, consequently requiring for conversion into a solid product neither acid nor lime, but merely evaporation. The cost of evaporation may be reduced by regulating the quantity of liquor condensed in the separator, and by circulating the liquor until of satisfactory strength for evaporation. The gases are forced through the saturator by the exhausters *b* and *c*, and are then cooled and passed to the benzol plant.

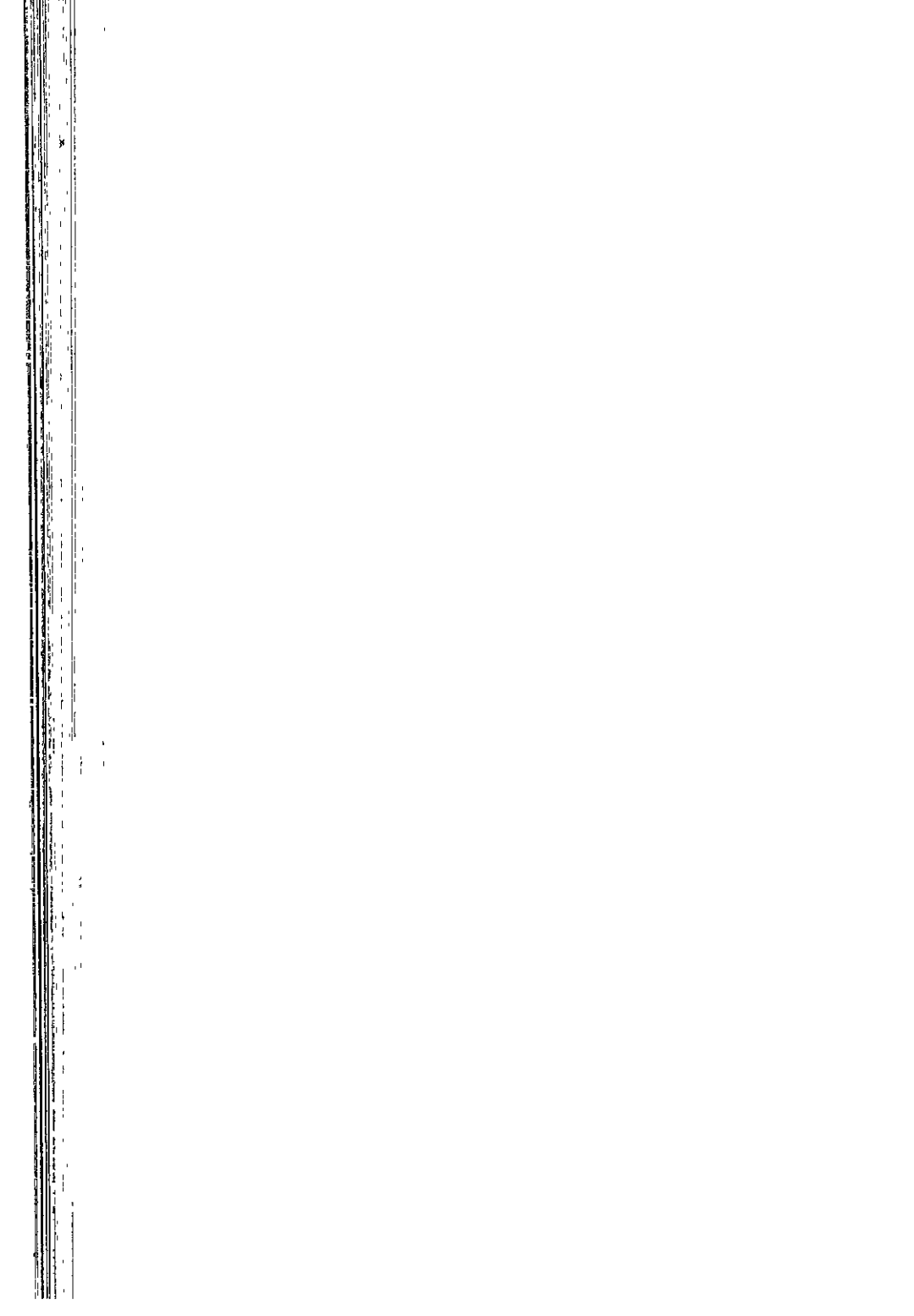
In the Simplex direct recovery system the gas is first treated by hot tar in a scrubber, the temperature of the tar being carefully controlled by allowing a definite proportion of hot tar to be pumped back to the scrubber. The lighter tar still in suspension is removed in a second tar extractor, utilising a centrifugal system. In this extractor the gas is drawn through a series of vertical tubes, each tube having a special cap with tangential slots. A high rotary motion is imparted to the gas, which thus strikes the interior surface of these tubes, causing the finer particles of tar to unite in sensible drops which flow down the pipe and are collected through a seal. The velocity of the gas is important, and is maintained by using blank caps, if necessary, to reduce the total area of the gas passages according to the output of gas, whilst the slots are kept clean by tar from a rotary distributor.

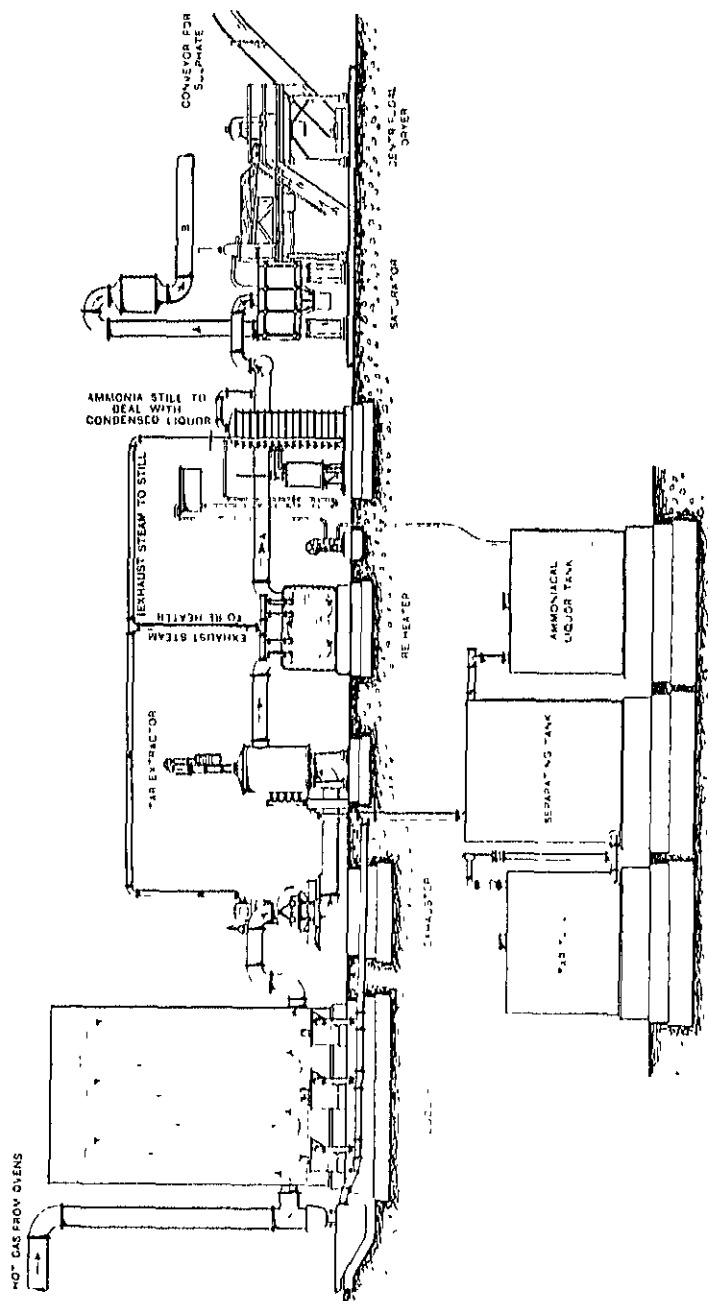
The Koppers process is shown in Fig. 33. The hot gas from the ovens enters a series of water-coolers of the tubular type, being thereby cooled to atmospheric temperature, and



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depositing the bulk of tar and liquor by condensation. The gas is then drawn by an exhauster and driven forward to a tar extractor of the impact type (vertical or horizontal), in which the last traces of tar are eliminated.

After leaving the extractor the gas passes through a reheater, where it becomes heated to such a degree as to permit of the gas being delivered direct into the saturator. The ammonia is extracted by direct absorption, and the sulphate produced is ejected in the usual manner. Any liquor produced in the preliminary coolers is treated in a still with addition of lime, the heat for this and for the reheater

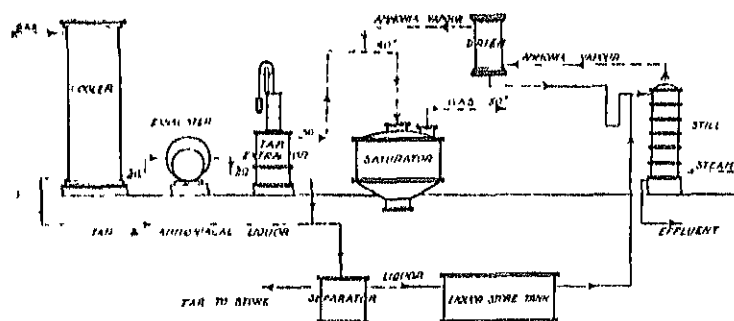


FIG. 31. Coppée Ammonia Recovery System.

being supplied by the exhaust steam from the engines driving the exhauster.

In the method adopted by the Coal Distillation Co., the gas is cooled in the usual manner, and the last traces of tar eliminated in a Pelouze and Audouin extractor. The compression of the gas in the exhauster raises the temperature about 10° , and this addition, along with the heat of reaction in the saturator, prevents condensation of water vapour in the saturator. The after-treatment of the gas is on the lines already indicated. If the gas is required for lighting purposes, the vapours from the ammonia still, being rich in sulphur compounds, are fed into a separate division of the saturator, and the foul gases are led away by a special curtain and are not introduced into the gas stream.

The Coppée process (Fig. 31) is conducted on similar lines,

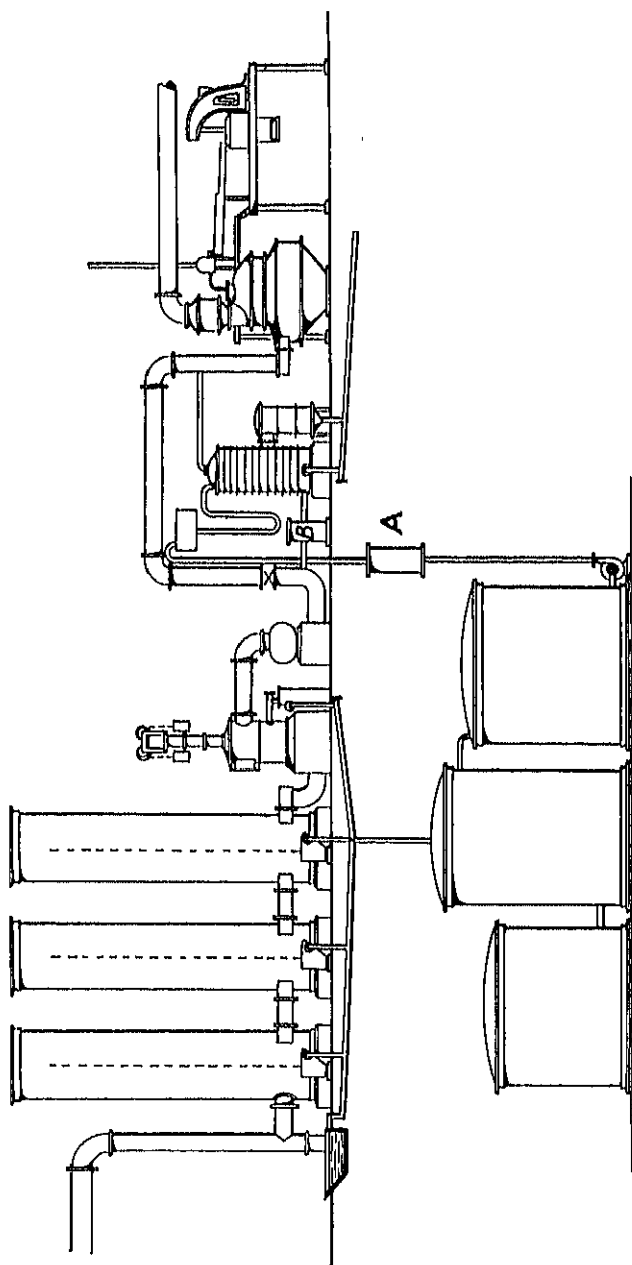


FIG. 36.—BRITISH COKE OVEN DIRECT RECOVERY PLANT.

from the main stream by a throttle valve after the exhauster. This subsidiary stream of gas is heated in a gas reheater B by means of flue gases. Thus no steam is required, and the ammonia vapours from the still pass into the main gas stream, which is then treated in the manner already described.

Messrs Bagley, Mills, & Co. (Fig. 37) utilise the principle of heat transference by actual contact between gas and liquor on lines somewhat similar to those applying in the case of the ammonia recovery system in connection with Mond producer gas. The gas from the ovens is cooled in the condenser A, fitted with a series of perforated baffle plates. Cold liquor is admitted by sprays at B, and owing to the counter-current

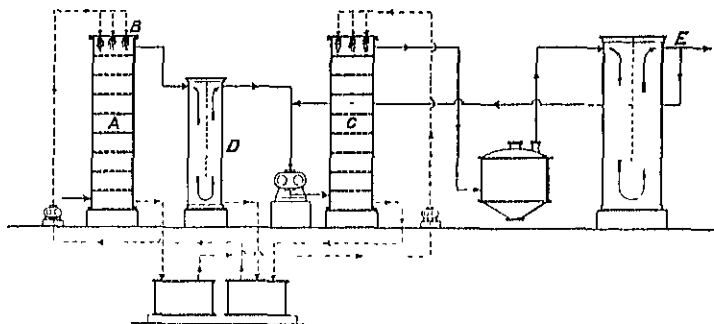


FIG. 37 - Bagley, Mills, & Co.'s Direct Recovery Plant.

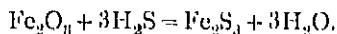
system, the intimate contact cools the gas from 100° to approximately 35° C., becoming itself heated from about 25° to 90° C. The hot liquor is separated from the tar and is sprayed into the vessel C, in which the heat thus abstracted in the first vessel is returned to the gas, which is raised in temperature to about 80° C., whilst the liquor is again cooled to about 25° C. Any free ammonia is taken up by the gases, which in a fully saturated condition enter the saturator. If these two vessels alone were used it is obvious that the liquor would gradually become hotter until the efficiency of the condenser A as a cooler and tar extractor would disappear. The equilibrium is, however, maintained by an intermediate cooler D, in which the gas temperature is controlled by external water circulation. Free ammonia is retained in the gas, whilst

the circulation of the liquor results in a solution containing fixed ammonia compounds, which may occasionally be treated for recovery of ammonium chloride. The water vapour originally in the hot gases is condensed, but revaporised in C to an extent governed by the temperature at the exit. The difference would have to be removed occasionally, but by by-passing some of the cooled gas to the system at E a larger quantity of water vapour can be carried, the efficiency being increased by reheating this branch stream if desired.

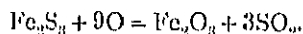
In the preceding processes sulphuric acid is required and, in the great majority of cases, is secured from external sources. Apart from the additional expenditure incurred, this state of affairs is much to be regretted from the standpoint of national economy. In the majority of cases there is sufficient sulphur in coke oven gas at any plant to more than satisfy its requirements of sulphuric acid, but with very few exceptions the sulphur is not recovered. It is probable that with a more extended field for coke oven gas for lighting and power a greater proportion of this sulphur will be recovered in the ordinary method of purification by oxide of iron. This method is an intermittent, and attempts have been made to recover the sulphur in a continuous method and in a condition capable of combining with the ammonia in the gas. A successful process on these lines and on a commercial scale would have more claim to the title of a "direct" process than any previously mentioned, but although the Burkheiser and Feld processes aim at this laudable object, they have not yet obtained a foothold in coking practice. In the Burkheiser process the gases are washed with water containing finely divided oxide of iron in suspension. Iron-sulphur compounds are produced, as well as soluble alkali polysulphides and sulphocyanides. The solid sulphides are recovered, dried, and roasted, giving a mixture of SO_2 and SO . The gas from the oxide of iron washer passes through a saturator charged with acid ammonium sulphite, which absorbs the ammonia, forming a mixture of normal ammonium sulphite and ammonium sulphate. A portion of the normal sulphite is utilised to absorb the SO_2 and SO from the roasting process, becoming converted into acid sulphite, which passes to the main saturator, and thus acts as the agent whereby the

sulphur compounds in the gas are made to absorb ammonia in a self-contained process. The salt produced is oxidised by air to ammonium sulphate. The reactions are complex, but may be summarised as follows:—

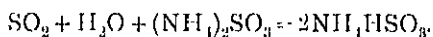
Absorption of H_2S :—



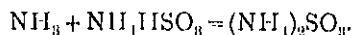
Regeneration of iron compounds:—



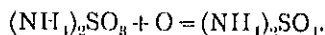
Transference of SO_2 :—



Absorption of NH_3 :—



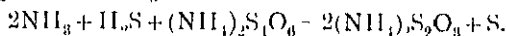
Oxidation of sulphite:—



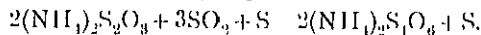
In the Feld process the gas is washed with a solution of ammonium polythionate which absorbs ammonia, becoming itself converted to ammonium thiosulphate accompanied by deposition of sulphur. The thiosulphate is regenerated by treatment with SO_2 and again passes to the ammonia absorber. The ammonia content of washing liquor gradually increases, and a portion is removed from time to time and treated for the recovery of ammonium sulphate.

The reactions may be indicated thus:—

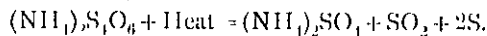
Absorption of NH_3 :—



Regeneration of washing liquor:—



Conversion to sulphate:—

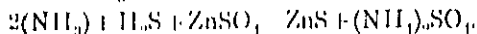


The SO_2 is used for further regeneration, the sulphur is filtered off and converted to SO_2 , whilst the solution of ammonium sulphate is evaporated under vacuum for the production of crystals.

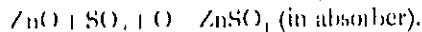
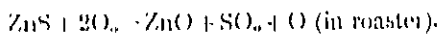
Another process has recently been introduced by Professor J. W. Cobb, Leeds University, in which it is proposed to wash the gas with a solution of zinc sulphate, the ammonia being

retained as a solution of ammonium sulphate, the zinc being precipitated by the H_2S in the gas as zinc sulphide. The latter, on roasting in air, forms sulphate and oxide, liberating sulphur oxides which are blown through water containing previously roasted material in suspension. The zinc is thereby reconverted to a solution of zinc sulphate and is reused, thus completing the circuit. The reactions may be thus summarised:-

Absorption of NH_3 :-



Regeneration:-



CHAPTER VII

DISTILLATION OF TAR

THE coal tar obtained at coke works is a black viscous fluid of a specific gravity usually varying from 1.1 to 1.2. It consists of a very complex mixture of compounds, chiefly hydrocarbons, but in some cases associated with oxygen, nitrogen, sulphur, etc. The manner in which these elements combine is uncertain, the nature of the compounds being largely influenced by the temperature of the coke oven. The yield of tar varies considerably, being mainly dependent on the nature of the coal treated and the temperature of the retort. The constituents of tar may be grouped as :—

1. Hydrocarbons—(*a*) Paraffin series, (*b*) Benzene series.
2. Bodies containing oxygen, tar acids, etc.
3. Bodies containing nitrogen, ammonia, pyridine, etc.
4. Bodies containing sulphur.
5. Pitch.
6. Free carbon.

The proportion of the above groups is not by any means constant, but depends very largely on the temperature to which the coal has been subjected. The effect may be better understood by considering two actual temperatures of coal distillation on a commercial scale. Dealing with a low temperature (about 500° C.) as in coalite processes, etc., the tar is recovered in greater quantity, amounting to about 20 gals. per ton of coal, and is very fluid as well as of low specific gravity. It is rich in hydrocarbons of the paraffin series, which are valuable as solvents and motor spirit, but is deficient in benzene hydrocarbons, hence is of little value to the dye industry. This low temperature tar is rich in tar acids, but has a comparatively low content of pitch. This is compensated for, to some extent, by the better quality

of this pitch, which possesses an exceedingly low content of free carbon, rendering it much more valuable for insulation purposes, etc. With cannel coal, even at higher temperatures, the tar usually contains paraffin bodies. At higher temperatures the tar recovered is not so fluid, is lower in the light oil fraction, contains more pitch of lower quality, and is recovered in less quantity, averaging about 10 gals. per ton of coal. Typical analyses of tars obtained at different temperatures are shown below:—

COMPOSITION OF TAR BY WEIGHT.

Ammoniacal liquor	-	-	1.20	1.03	1.01	1.01	0.38
Crude naphtha	-	-	9.17	9.65	3.73	3.45	0.99
Light oil	-	-	10.50	7.46	4.47	2.59	0.57
Creosote oil	-	-	26.45	25.83	27.29	27.33	19.41
Anthracene oil	-	-	20.32	13.47	18.13	13.77	12.28
Pitch	-	-	28.29	36.80	41.80	47.67	64.08
Specific gravity	-	-	1.08	1.10	1.11	1.15	1.20
Approximate temperature	-	600° C.	700° C.	850° C.	950° C.	1,100° C.	

—L. T. Wright.

The constituents of tar have widely varying boiling points, some of the more important being described below:—

Constituent.	Boiling Point.	Formula.
	° C.	
Benzene	80.5	C_6H_6
Toluene	110	C_7H_8
Xylene	138 to 142	C_8H_{10}
Naphthalene	218	$C_{10}H_8$
Anthracene	360	$C_{14}H_{10}$
Pyridine	117	C_5H_5N
Carbolic acid	181	C_6H_5O
Cresylic acid	188 to 200	C_7H_7O
Carbon disulphide	47	CS_2
Thiophen	81	C_4H_2S
Aniline	182	C_6H_5N

By reason of the difference in the boiling points of the various compounds, tar may be readily split up into groups of compounds by fractional distillation, a rough separation

being obtained by collecting the distillates at the following temperatures to form definite "fractions"—

1. "Light oil" - - Collected up to 170° C.
2. "Middle oil" - - " between 170° and 230° C.
3. "Heavy oil" - - " " 230° and 270° C.
4. "Anthracene oil" - - " " 270° and 360° C.
5. "Pitch" - - - Residue left in retort.

Though a laboratory method on a small scale may indicate

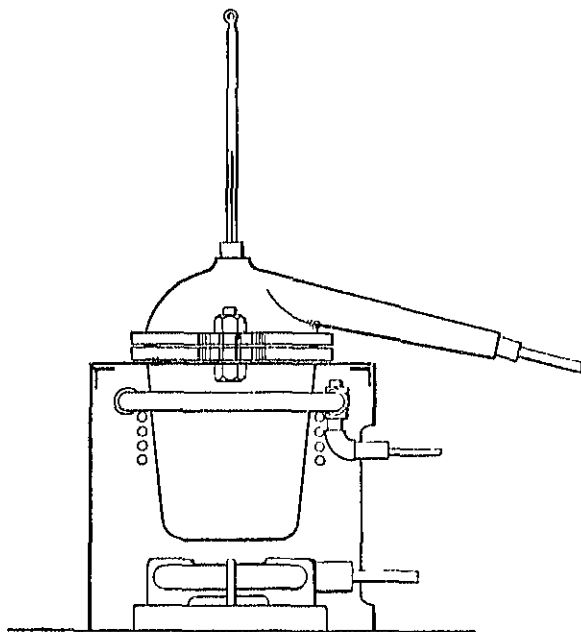


FIG. 38.—Tar Retort.

comparative results, it is scarcely satisfactory in estimating yields of various fractions obtainable on a large scale, though it is very often convenient to make use of laboratory tests as an approximate guide to the nature of the material being dealt with. Whenever possible, a small still capable of dealing with, say, 100 gals. is much to be preferred. If this is impracticable, a useful test may be done on a laboratory scale with apparatus such as shown in Fig. 38. At least 1 litre of tar should be used.

The retort is of iron, with suitable flanges for making a gas-tight joint, and a small opening in the upper part for the insertion of a thermometer. The retort is either supported on a sheet-iron screen which surrounds the lower part of the retort, or stands on a strong tripod inside the screen. Round the upper portion of the retort, below the flanges, a ring burner is fixed which serves the very useful purpose of first heating the upper portion, and driving off the water without frothing. Another burner is placed under the base of the retort, and serves for the distillation proper. It is advisable,

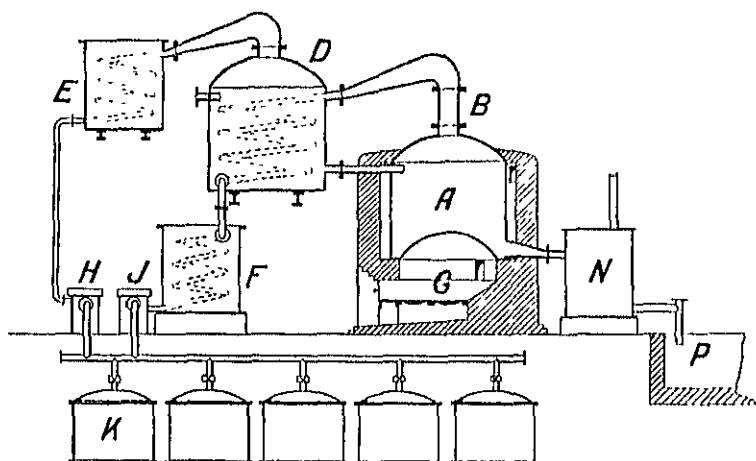


FIG. 39.—General Arrangement of Tar Distilling Plant.

in the earlier stages of the distillation, to keep the retort neck as cool as possible. The whole is connected to a suitable condensing apparatus: in many cases a long iron (or glass) tube is sufficient. After the light oil stage the retort neck may be allowed to warm up to prevent blockages from naphthalene, and in the later stage (*i.e.*, anthracene) this outlet tube may require to be warmed externally to keep the distillate liquid. The various distillates may be measured, and the pitch, whilst still fluid, may be poured into a tared dish and weighed when cold.

A typical plant for the distillation of tar on a commercial scale is shown in Fig. 39, a tar still in detail being shown in Fig. 40. The still *A* is constructed of mild steel plates, the

bottom being dished to present a greater area to the heat from the grate *G*. The flame, after passing underneath the still, rises in a spiral direction round the sides and passes into the chimney flue through an opening fitted with a damper. The vapours evolved pass off through the cast-iron swan-

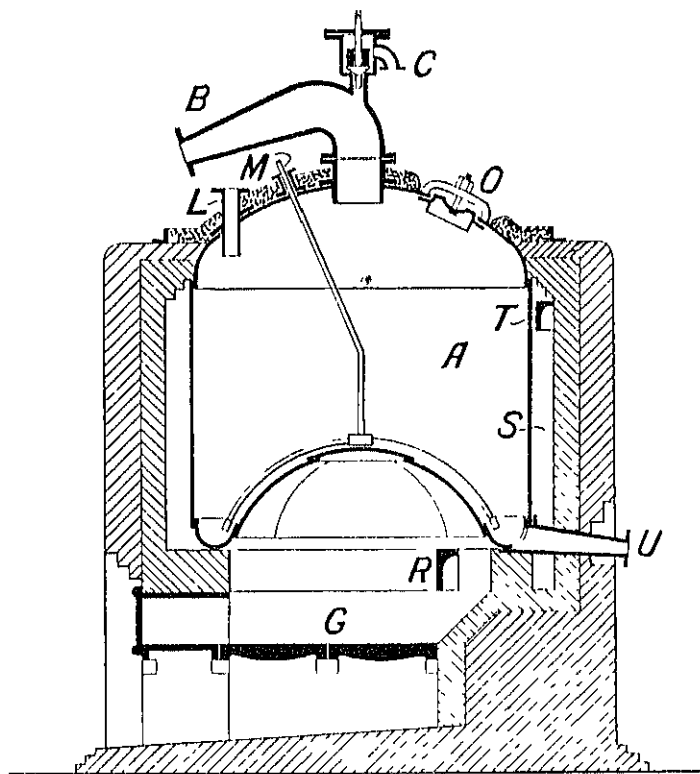


FIG. 40. --Tar Still.

neck fitted with a safety valve *C* into a coil passing through a primary still *D*. This primary still has been previously filled with cold tar, which thus becomes preheated by the hot vapours from *A*. By utilising two stills in this manner considerable economy is effected, and the water and a portion of the lighter oils in the primary still pass off and are separately condensed in the cooler *E*. The vapours from the main still, after passing through the primary still, are completely con-

densed in F. The products from these coolers pass through inspection overflow boxes H and J to any desired store tank K, according to the number of fractions desired, the "change over" point being usually determined by the specific gravity of the distillate. After the light oils have passed over, the water in the condenser F is shut off, allowing the temperature to rise, as otherwise naphthalene, which is solid on cooling, would obstruct the pipes. The successive fractions are taken, and towards the end of the distillation steam (which must be dry) is blown into the still through the distributing pipe M (Fig. 40), to assist in the expulsion of the oils of high boiling point, and to prevent the formation of carbonaceous residue on the bottom of the still. When tests show that the liquid fractions are expelled as far as desired (according as hard or soft pitch is aimed at) the fire is drawn, and after a few hours' cooling the pitch in a molten condition is run off into the cooler N, the fumes from which pass into a purifier. The main still is then refilled with tar, already in a heated condition and deprived of water and light oils, from the primary still, which in turn is filled with cold tar, and the process is continued.

After a time, when the evolution of acrid fumes has ceased and the pitch is still liquid, the contents of the pitch cooler are run off into pitch bays P, and allowed to solidify.

In some cases tar is prepared for the treatment of roads as a constituent of tar macadam or for surface tarring. The specifications of tar for this purpose, as issued by the Road Board in their "General Directions relating to the Tar Treatment of Roads," are given below :—

	No. 1. Surface Tarring.	No. 2. Tar Macadam.
Below 170° C. - - -	Under 1 per cent (exclusive of water)	Under 1 per cent (light oils + water)
170° to 270° C. - - -	16 to 26 per cent	12 to 18 per cent.
270° to 300° C. - - -	3 to 10 "	6 to 10 "
Total between 170° and 300° C	21 to 31 "	21 to 26 "
Free carbon - - -	12 to 21 "	12 to 22 "
Middle oils to be free from naphthalene at - - -	30° C	25° C.
And to contain tar acids -	Under 3 per cent.	Under 2 per cent.

Usually a distillation of the tar up to the removal of water and light oil is sufficient, and the process is much simplified.

The process described is an intermittent one, but various attempts have been made to distil the tar in a continuous fashion with more or less success. In some of these systems the tar passes through a series of stills in comparatively thin

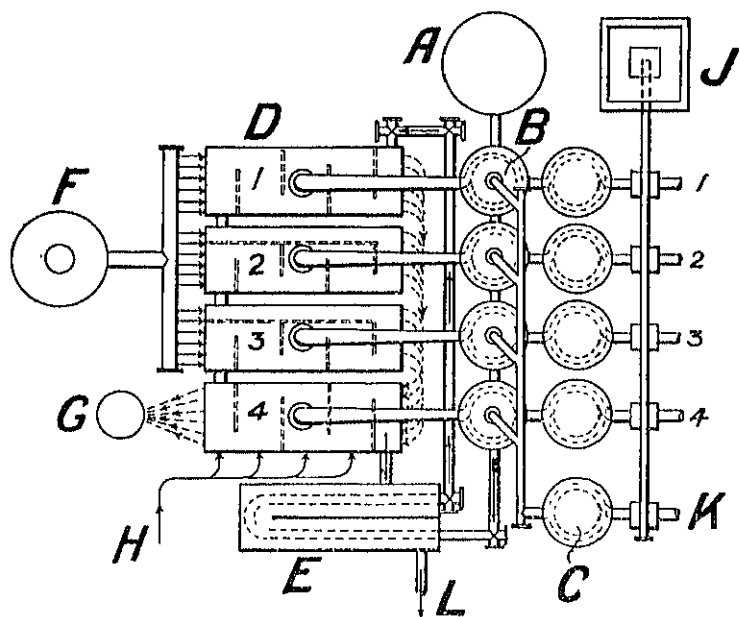


FIG. 41.—Continuous Tar Distilling Plant. (W. C. Holmes & Co.)

layers. These stills are maintained at successively higher temperatures, so that light oils are expelled in the first vessel, middle oils, etc., in the second, and so on. The various distillates are condensed in separate coolers. In some cases the tar is heated in a serpentine coil until a pitch temperature is reached. The mixed vapours are then fractionally condensed, heavy oils coming down in the first condenser, light oils in the second. Again tar, after preheating, may be sprayed into a vessel in a finely divided state and treated with superheated steam. Under these conditions the high boiling constituents

distil over at lower temperatures, molten pitch being run off continuously. Sometimes a continuous plant or a portion of it is worked under a vacuum to bring the oils over at a lower temperature. In all cases there is a considerable amount of heat carried away, first by the vapours passing off at increasing temperatures, secondly by the hot molten pitch, and an economical continuous process must rely largely on a satisfactory recuperation of this heat. A good example of this is shown in the Hird continuous process (Fig. 41, W. C. Holmes & Co., Huddersfield). In this plant the tar from the store tank passes through four heater-condensers in succession, meeting in each case a gradually increasing temperature from coils through which vapours from the stills are passing. Owing to the somewhat lengthened contact the tar becomes heated sufficiently to give off vapours in these vessels, the vapours uniting in a common collecting main and being condensed in the water-cooled vessel K. A further exchange of heat occurs in the pitch cooler. . . . Here the pitch is cooled sufficiently to be discharged directly into the pitch bays, whilst the incoming tar receives a further addition of heat. The tar, now already in a heated condition, passes through a series of horizontal stills D1, 2, 3, and 4, its course through these stills being lengthened by baffles. The tar is heated in the first three vessels by producer gas or coke oven gas, the burner tubes being embedded in the tar. The tar is in shallow layers, no portion of it being more than six inches from the source of heat, whilst the vapour space above the tar is amply proportioned. In the fourth vessel the products of combustion from the first three stills supply the heat, whilst the expulsion of the anthracene oil is assisted by steam injected at H. The vapours from each still pass through their corresponding heater-condensers, and are thus economically partly cooled, the final condensation being brought about in the water-cooled vessels K1, 2, 3, 4, etc. The condensates pass through the various seal boxes as shown to their respective store tanks, any foul gases being passed through the purifier. It will be seen that in certain specifications issued by the Road Board, one of the constituents specified is free carbon, from which it evidently is regarded as an important factor in the durability and

binding qualities of tar used in road making material. Its estimation may be made by dissolving out all the soluble constituents of the tar by means of solvents such as benzol, carbon disulphide, pyridine, xylol, alcohol, aniline oil, etc.

The authors have found an ordinary Soxhlet apparatus very suitable for the purpose. Ten gm. of the tar to be tested are weighed off into an ordinary filter thimble, which is placed in the upper part of the Soxhlet: the flask is half filled with benzol, and heat applied by means of a water bath on which the flask rests. The benzol is volatilised, and passes up into the higher portion of the apparatus through a side tube, where it condenses and drips into the thimble containing the tar. In time the liquid reaches such a level in the extraction part as to siphon over again into the bottom flask, and the whole process is repeated. This should be allowed to go on until the liquid siphoning over is practically colourless. Now substitute pyridine for benzol in the lower flask and repeat the extraction. Additional heat will be required, and a bath of linseed oil is used instead of water. After several pyridine extractions substitute methylated spirit, and extract as previously until colourless. Finally take out the filter thimble, dry in water bath, and weigh. Instead of using the Soxhlet apparatus, good results may be obtained by direct treatment on an ordinary filter paper in a glass funnel, washing with hot benzol, or xylol, pyridine, and alcohol in succession, until the final washings are colourless. The authors have used both methods with fairly concordant results.

The specific gravity of tar varies considerably, and may be ascertained by means of an ordinary specific gravity bottle, but this is a tedious and messy operation. It can be got much more readily, and with sufficient accuracy for practical purposes, by means of a Twaddell hydrometer. Even then it is by no means easy unless the tar is warmed to make the tar more fluid. The authors find that a temperature of 120° F. is suitable, making an addition of 1 degree Tw. for every 10° F. above 60° F. An illustration of this hydrometer is shown in Vol. I., also the manner in which degrees Tw. are converted into specific gravity figures.

A metal hydrometer (nickel plated copper or nickel silver) is preferable to one made of glass, because of the rough usage

it is liable to receive. It should be noted that the specific gravity of a tar is not by itself a sufficient indication of the utility of the tar.

With regard to the viscosity of tar, the ordinary methods of viscometry, which depend chiefly on measuring the rate of flow of the fluids (oils, etc.) through an orifice of standard size, are not suitable. An instrument very similar to a hydrometer is used, and its rate of penetration in the tar between definite points on the stem of the instrument is taken as a measure of the viscosity of the tar, and carefully manipulated, gives results sufficiently accurate for practical purposes. Several tests should be made, and the mean result taken. Temperature is a most important factor, and the test should be made at 59° F. Naturally the viscosity decreases with rise in temperature, and vice versa.

CHAPTER VIII

BENZOL

THE term "Benzol" as applied to coking practice is used in a rather indiscriminate manner. Certain definite chemical compounds, each with decided characteristics, enter into its composition, but in general we may look upon benzol as a mixture of compounds of the aromatic series of the general formula C_nH_{2n-6} associated with certain impurities. The compounds of importance in benzol are:—

Main products	Benzene	C_6H_6 —Boiling point, 80.5° C.
	Toluene	C_7H_8 " 110.0° C.
	Ortho-xylene	C_8H_{10} " 142.0° C.
	Meta-xylene	C_8H_{10} " 139.0° C.
	Para-xylene	C_8H_{10} " 138.0° C.
	Propyl-benzene	C_9H_{12} " 160.0° C.
Impurities	Carbon disulphide	CS_2
	Thiophene	C_4H_4S
	Thiotolene	C_8H_6S
	Paraffins	C_nH_{2n+2}
	Phenols	C_6H_5OH
	Pyridine	C_5H_5N
	Naphthalene	$C_{10}H_8$
	Cresote oil,	
	Cumaron and other resinous matters	

The general scheme of benzol recovery may be divided into the following headings —

- (a) Extraction of a complex mixture of aromatic hydrocarbons and associated impurities by treating the gas with solvents of higher boiling point.
- (b) Expulsion of this mixture from the solvent by regulated heat treatment.

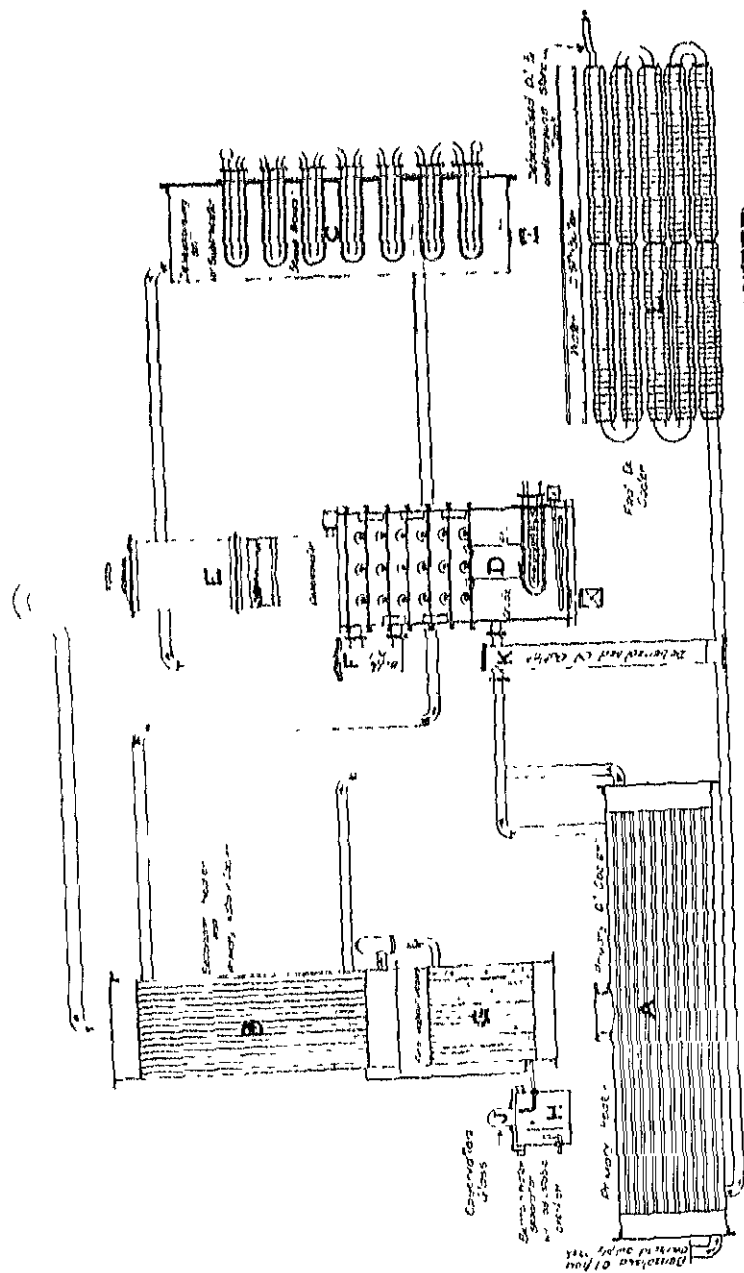
- (c) Preliminary fractionation into groups of compounds according to the respective boiling points.
- (d) Chemical treatment of the various fractions.
- (e) Redistillation and careful fractionation of the chemically treated products.

With reference to the first heading, the crude products could be extracted by cooling the gas to a very low temperature whilst subjecting it to a high pressure, but owing to the relatively small proportion of benzol vapours in the gas, and consequently the large volume of gas to be thus treated, this process is too costly to work under ordinary circumstances, and the method usually adopted is to scrub the gas with an absorbent. The apparatus used may be of the tower type, rotary type, centrifugal type, or intensive spray type, which have already been described in the chapter dealing with ammonia recovery. For absorption purposes blast furnace creosote may be used, but whilst it has an advantage in being free from naphthalene, there is a risk of the benzol produced being contaminated with paraffin compounds, an important point in benzol required for nitrating purposes and aniline manufacture.

The great majority of plants use some form of coal tar oil as a scrubbing agent, creosote being generally preferred. The quality of the oil used is of the highest importance, and periodical tests should be made to ensure a requisite standard being maintained. A good wash oil should be fluid, free from water, light oils, and naphthalene as far as possible, and of satisfactory distillation test and specific gravity. A good specification for a suitable oil would be:—

Specific gravity:—1.03 to 1.05. Retort test with bulb of thermometer in the liquid:—No distillate below 200° C., 70 to 90 per cent. between 200° and 300° C. The distillate up to 300° on cooling to 10° C. should not show more than 7 per cent. of solids. The writer would prefer a wash oil with a distillate up to 300° C. approaching the lower limit given, as this allows a certain proportion of anthracene or "green" oil to be introduced. This tends to bring about a cleaner separation of the crude benzol at a later stage, whilst the viscosity of the oil, though thereby increased, does not

seriously affect the working of the plant. As to the amount of wash oil circulated, figures of 50 to 120 gals. of wash oil per ton of coal have been given, the writers' experience being in favour of 90 gals. of oil circulated per ton of coal, the benzolized oil containing about 3 per cent. of crude benzol. A portion of the wash oil should be removed from circulation from time to time and replaced by fresh oil, as the oil tends to thicken, with a decided deterioration in absorbing power. The wash oil is usually circulated through two or three scrubbers in series, and in the opposite direction to the flow of gas, the final gas being treated with the debenzolized oil, which thus absorbs the benzol in stages, and after circulating through the system, passes to the distillation plant as benzolized oil. The extraction of benzol from the enriched oil depends mainly on the application of heat. Thus it could be readily driven off in a pot still by an open fire, and in fact a tar dehydrating plant has been successfully used for this purpose. In dealing with the comparatively large volume of benzolized oil obtained at an average coke plant, a continuous process of distillation is preferred, enclosed and open steam being the heating agent in this case. The hot debenzolized oil after satisfactory cooling is reused in the scrubber, thus completing the circuit. The hot benzol vapours, excess of steam, and debenzolized oil carry away considerable heat from the still proper, and a modern plant aims at the recovery of as much of this "spent" heat as possible, transferring it by means of preheaters to the incoming "saturated" oil. The principle of one type of modern debenzolizing and absorption plant is shown in diagram form in Fig. 42. Wash oil is pumped from the scrubbers to elevated store tanks, from whence it flows by gravity through the debenzolizing system. In this type the oil is preheated in three stages, first by means of hot debenzolized oil in the heater A, secondly by hot benzol vapours and excess steam in B, thirdly by enclosed steam coils in the heater C. The oil, heated to about 110° C., passes into the main still D, constructed on the principle of an ammonia still, and passing over successive trays, is agitated thoroughly by steam admitted in the lower part, and the benzol is expelled. This agitation with open steam is necessary if we wish to strip the oil satisfactorily,



CRUDE BENZOL PLANT BY R. & J. DEMPSTER LIMITED.

FIG. 42.—CRUDE BENZOL PLANT. (By R. & J. Dempster, Limited.)

but at the same time the tendency for the more volatile products to carry forward a portion of the heavier oil is increased, and in addition to the lighter products an appreciable proportion of creosote oil and naphthalene pass forward. Accordingly a fractionating column E is attached to restrict the passage of these mixed vapours, and by atmospheric cooling to selectively condense some of the higher boiling products. The ascending vapours are made to bubble through the descending condensate, and the separation of the products is rendered more complete. The vapours leaving this column pass through the condenser heater B, and are finally condensed in the water-cooled condenser C. The mixture of water and crude benzol passes to the separator H, in which the water is siphoned off from the bottom, whilst the crude benzol is run off from the top to the store tank. The hot debenzolized oil from D passes through the preheater A, and is finally cooled by a water-cooled system of piping at L, passing thence to the absorption system.

The above diagram is given to show the general principle, but the types of crude benzol plants in vogue vary considerably as to the relative disposition of the several units. Thus in some cases, instead of an atmospherically cooled column E, a multitubular cooler is superimposed, cold benzolized oil flowing round the outside of the tubes, and regulating the temperature of the vapours passing through. In some cases the incoming oil is preheated by benzol vapours only, whilst sometimes a separate steam heater is dispensed with, in which case a somewhat larger main still is used with enclosed steam coils in some or all of the tray sections. Again the preheater, condenser, and separator may be superimposed. It is important in the working of a crude benzol plant that ammonia be satisfactorily removed before the entry of the gas into the benzol scrubbers. If not completely removed, any water in the wash oil absorbs the ammonia compounds which are decomposed in the steam preheater, the liberated acids attacking the heating coils, more especially if the latter are of wrought iron or steel. The writer has known cases in which cast-iron coils have been destroyed in a few weeks, a solid deposit in the heater indicating a corrosion due mainly

to the formation of iron sulphide. The evil may be mitigated somewhat by keeping the water content of the oil at its lowest limit, a final heating of the oil by a closed steam coil in close proximity to the open steam jets being sometimes advantageous in this respect. In all cases heating coils should be arranged to permit of easy access for examination or removal. A perforated heating coil gives rise to a sudden increase in the amount of open steam, with a consequent priming of the still, or a sudden reduction in the distillation test indicating a higher proportion of heavier products carried over mechanically. If not remedied immediately, there is a risk of water passing into the oil, and the corrosion would be intensified. At some works crude benzol only is produced, and to avoid carriage by rail of an undue proportion of wash oil in the benzol, a distillation test is usually stipulated, a very common specification requiring a distillate of 65 per cent. when heated in a retort to 120°C . If the crude product is to be worked up at the coke plant, this test is not necessary, and it is usually an advantage to work the crude benzol plant to give a benzol of lower distillation test, often as low as 50 per cent. at 120°C . The after-treatment of the crude benzol is dependent on the class of products sought. In a few cases it is split up into products each of certain range of distillation, but without chemical treatment. More commonly it is rectified by distillation and chemical treatment, and split up into products in which benzene, toluene, and xylene predominate respectively. These semi-pure products in other cases are further chemically treated and fractionally distilled to form products more or less approximately to the definite chemical compounds: benzene, C_6H_6 ; toluene, C_7H_8 ; xylene, C_8H_{10} , etc. The majority of benzol plants aim at the production of products of the following designation and distillation test:—

90 per cent. benzol -	90 per cent. distilling over between	80° and 100°C .
90 per cent. toluol -	90 " " "	100° and 120°C .
Solvent naphtha -	90 " " "	135° and 160°C .
Heavy naphtha -	90 " " "	160° and 190°C .

The above may be "washed" or "unwashed" products,

but usually the former. Before the war the following specification was also in vogue :—

50-90 per cent. benzol - 50 per cent. at 100° C., 90 per cent. at 120° C.

And occasionally pure products were sought of specifications more or less approximately to :—

Pure benzene - 95 per cent. distilling over within 8° C. (now within 5°).

Pure toluene - 95 " " " 8° C. (" 5°).

Pure xylene - 95 " " " 3 to 4.5° C.

The above tests are made on a retort with the thermometer immersed in the liquid about three-eighths of an inch from the bottom (see later). The following tests are conducted in distillation flasks with side outlet, the bulb of the thermometer being in the path of the vapour just below the side tube, and are in accordance with requirements under present conditions.

Standard benzol - - At least 95 per cent. at 90° C.

Toluol - - 90 per cent. between 100° and 117° C.

Solvent naphtha - - 90 " " 130° and 160° C.

The first stage in the treatment of the crude benzol consists of a preliminary distillation, the main object being to separate the bulk of the wash oil and naphthalene. The whole of the more volatile products may be "blown over" in a preliminary still into one collecting tank, and the blown-over product, consisting of a mixture of benzol, toluol, and solvent naphtha, afterwards treated with sulphuric acid and caustic soda in a special washer. The washed product may then be fractionated into the respective washed products, benzol, toluol, etc. The more common practice is to exercise a certain degree of fractionation in the blowing over stage, splitting up the crude benzol into unwashed 90 per cent. benzol, toluol, and solvent naphtha fractions, etc. These products are then separately washed, and since the proportions of washing media vary considerably for these fractions, more efficient and economical washing is obtained. The washed products are then redistilled with a more or less severe fractionation according to the specification aimed at.

The general scheme of a benzol rectification plant is shown in Fig. 43. The still A is charged with crude benzol from the tanks 1 and 2, and is gradually heated by dry steam

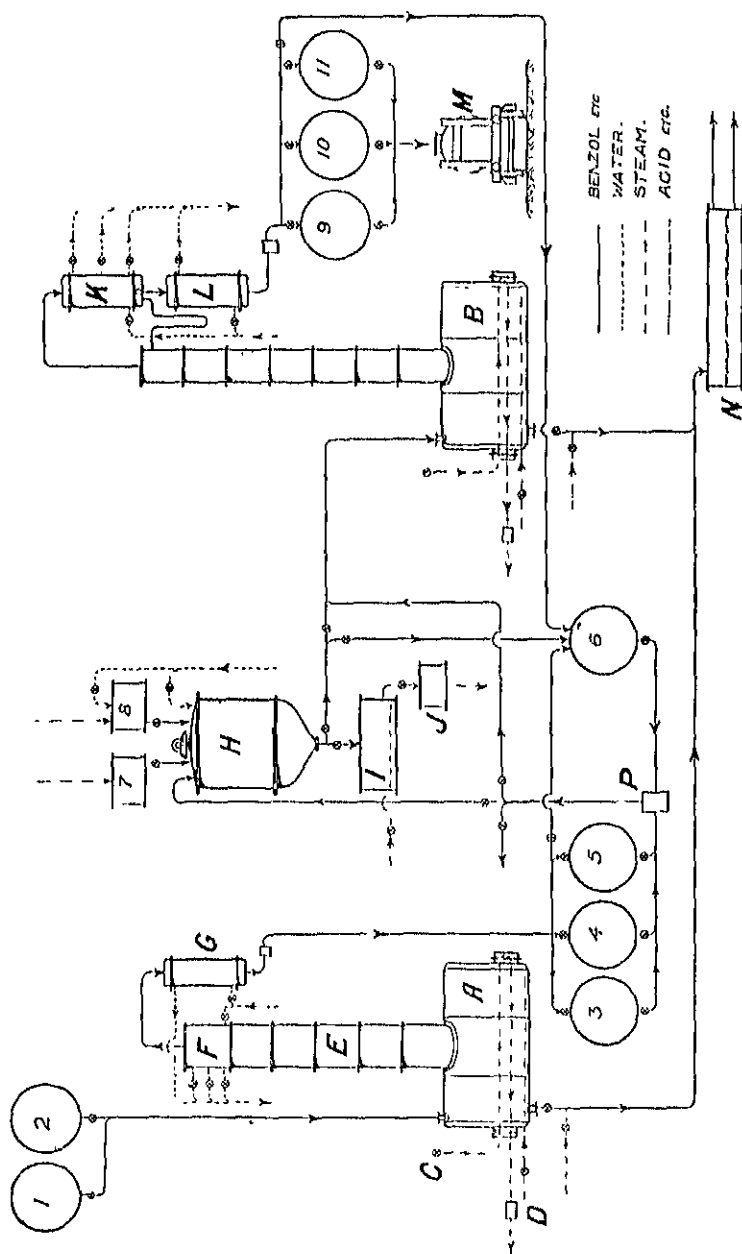
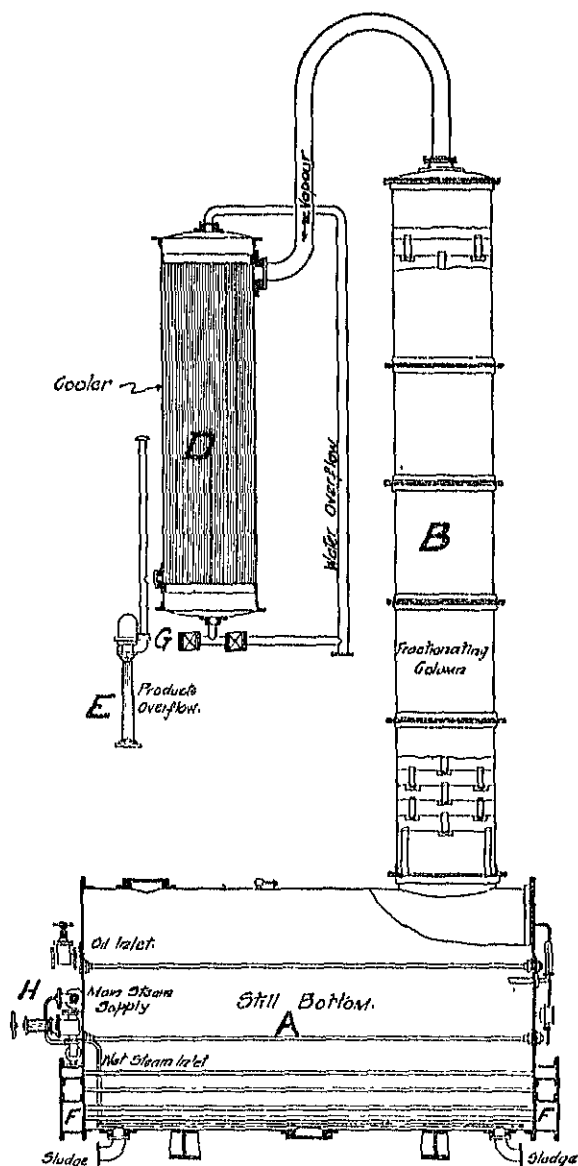


FIG. 43.—DIAGRAM OF BENZOL RECTIFICATION PLANT

at C, passing through a series of tubes adapted for easy removal in case of repairs, etc., the pressure being maintained by a steam trap. The first vapours expelled from the crude benzol contain a high proportion of carbon disulphide, and rise through the fractionating column R and the dephlegmating section F. The latter section consists of a multi-tubular cooler, water passing round the outside of a series of tubes, the benzol vapours, etc., rising upwards through the tubes. By regulating the flow of the cooling water a partial condensation of the vapours is brought about, only the most volatile compounds being allowed to pass. The vapours passing the section R are completely condensed in a condenser G passing through a visible overflow arrangement to any desired store tank 3, 4, or 5. In most cases the "first runnings" are isolated to reduce the proportion of carbon disulphide in the "blown-over" benzol. The products of higher boiling point selectively condensed in R pass back into the column R, and in their descent scrub out of the ascending mixture of vapours a considerable proportion of the particles of higher boiling liquids carried forward mechanically. In due course the first runnings are expelled, and the temperature of the still is allowed to rise, the products now coming away containing a large proportion of benzene, and giving on condensation an unwashed product in tank 3 suitable for working up into washed 90 per cent. benzol. When a distillation test of the condensate from G gives the necessary indication the temperature of the still is allowed to rise still further, the quantity of water flowing through R being at the same time checked so as to allow the temperature to rise, permitting the passage of higher boiling products. These on condensation give a liquid in which toluene predominates, and which is then diverted to the tank 4 for subsequent working up into washed 90 per cent. toluol. Similarly a naphtha fraction is next driven off, but in this case the temperature of the enclosed steam is not high enough, and open steam is admitted, the mechanical action assisting in the expulsion of the naphthas. Occasionally the still is worked under a vacuum. Simultaneously the water is cut off entirely from R, and the condensed product passes to 5, to be worked up later to solvent and heavy naphtha. After



PRIMARY FRACTIONATING STILL

R & J. DEMPSTER LIMITED.

FIG. 44.—PRIMARY FRACTIONATING STILL. (R. & J. Dempster, Limited.)



FIG. 45.—FINAL FRACTIONATING STILL. (R. & J. Dempster, Limited.)

a little experience with any particular make of crude benzol a good indication of the change-over points for these respective products may be obtained by allowing a certain volume of each product to come over before changing on to the next fraction. The residue left in the still consists mainly of naphthalene and wash oil, and is run to a cooling tank N in which, after cooling, naphthalene is deposited and removed by filtration, the clear oil passing to the wash oil store tanks. The crude products in 3, 4, or 5 are individually pumped to the washer H by means of the pump P. The washer consists of a lead-lined cylinder fitted with an agitating device. Here the product is washed by sulphuric acid, water, caustic soda, etc. Pyridine bases combine with the sulphuric acid, whilst phenolic bodies, olefines and unsaturated hydrocarbons form with the acid thick resinous substances which sink to the bottom. A portion of the thiophene is also removed. The duration of the agitation period, amount of acid and soda used, number of washings, etc., varies considerably with the quality of the crude products, scarcely two plants working under similar conditions. The following may, however, be given as an approximate guide:—

1. Wash one hour with 4 per cent. by weight of sulphuric acid, 168° Tw.
2. Rest one hour, and run off acid.
3. Wash one hour with 3 per cent. sulphuric acid as above.
4. Rest one hour and run off acid *very carefully*.
5. Gently wash the sides of the washer with water without agitation, and run off.
6. Wash with water twenty minutes with gentle agitation, and run off after one hour's rest.
7. Wash with 1 per cent. caustic soda, 10° Tw. half an hour.
8. Rest one hour, run off.
9. Wash with water as before.

The washer is fitted with a conical shaped bottom to allow the acid, etc., to be separated to the last drop. The thick spent acid is collected in tank I, in which it is agitated by live steam. This brings about a separation of the hydrocarbons,

partly by evaporation and partly by coagulation into a scum which may be removed in J by filtration, the filtered acid in some cases being used in the sulphate house. The washed products are conducted to the final rectifying still B, the treatment there being on lines similar to those obtaining in the primary still A.

The fractionation, however, is more drastic, a taller column being used, as well as a separate and larger dephlegmator K. The still is worked more carefully, especially in the vicinity of the change-over points. The washed products pass into tanks 9, 10 and 11 as washed 90 per cent. benzol, 90 per cent. toluol, 90 per cent. solvent naphtha, etc., and from thence, after a certain amount of mixing, if necessary,

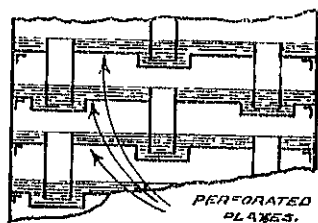


FIG. 46. Section of Fractionating Column.

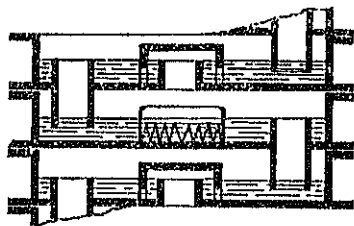


FIG. 47.—Section of Fractionating Column

to meet the required specification, are conducted to the tank wagon M. Tank 6 represents one or more reserve tanks to facilitate the reworking up of doubtful products due to pining, etc.

If pure products (boiling within $^{\circ}\text{C}$., etc.) are desired, more prolonged acid washing is necessary, and a further redistillation, greater care being exercised in controlling the temperature and rate of distillation. The fractionating columns used in connection with benzol recovery are usually of the perforated plate type (Fig. 46), or of the bubbling hood type (Fig. 47). The plate type consists of a series of perforated plates as shown, dip-pipes and cups being fitted to allow the condensed liquids to flow back to the still. The dip-pipes are fixed so as to maintain a certain depth of liquid on each plate, and the ascending gases are well distributed by the perforations in the plates.

The bubble type is designed on the lines of an ammonia still, and may be readily understood from the drawing.

The dephlegmator or analyser may be of the vertical multitubular type, as already described, in some cases having water outlets at different levels to assist in controlling the temperature.

Another type of analyser consists of a series of enlargements of the vapour pipe fitted horizontally in a water-cooled tank. Water enters and flows through the apparatus in the opposite direction to the vapour, so that the vapours farthest from the still are in contact with the coldest water. Any liquids condensing in these enlargements are run back into the column at different levels, the first condensate being admitted nearer the base of the column, the last condensate, consisting of more volatile products, re-entering the column nearer the top.

In the processes of rectification described an intermittent principle is adopted, but in the discussion on a paper dealing with benzol rectification¹ a description of the continuous method of the Coke Oven Construction Co. is given. The Solvay column used consists of a number of superimposed compartments containing hoods immersed a fair depth in the liquid. Oil is fed continuously into a compartment near the top of the column and passes downwards, steam admitted at the bottom bubbling through the several baths of liquid in the various compartments. The volume of liquid in the column and the quantity of feed are considerable enough to minimise any variations in the rate, temperature, or boiling point of the feed, and the results generally are less dependent on the skill of the operator. The greater depth of liquid in each tray brings about a more effective fractionation. To obtain two fractions one column may be mounted on top of another, the continuous feed then passing through both, and the fractionated vapours from each column being separately dealt with. The capacity of a column may be increased by adding more compartments, whilst low boiling impurities may be eliminated by isolating the vapours from

¹ "The Rectification of Benzol," W. Newton Drew, Midland Inst. of Mining, Civil, and Mech. Eng.

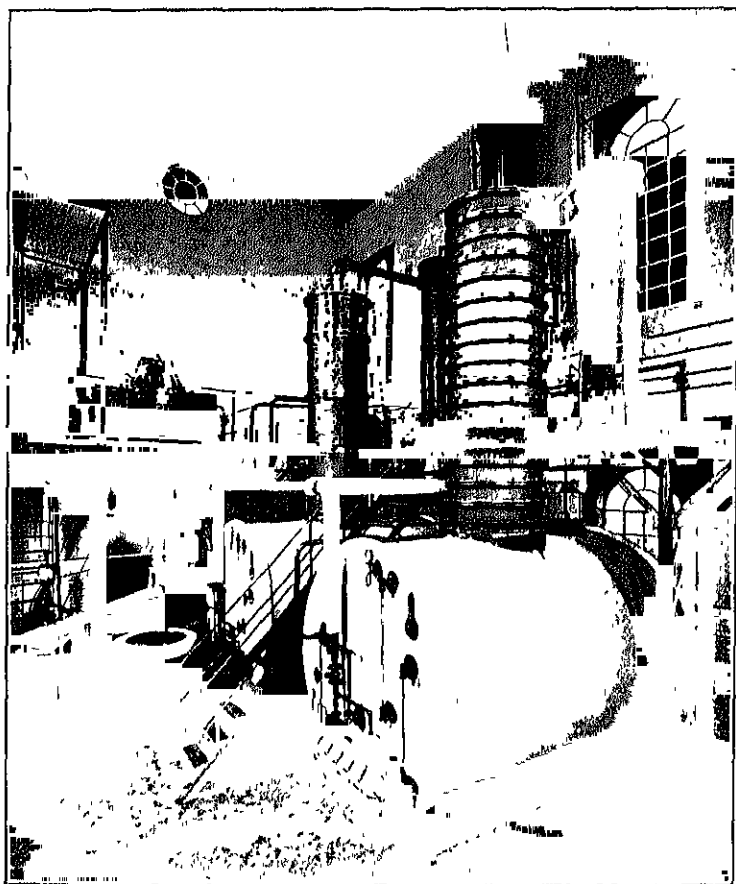


FIG. 48 — BENZOL RECTIFICATION PLANT (MES IS Simon Carves.)



several of the top compartments of the 90 per cent. benzol column.

The laboratory work in connection with a benzol plant is highly important. In the first place, the wash oil should be periodically examined and the efficiency of the scrubbers ascertained. The latter presents a certain amount of difficulty, as the volume of benzol vapours, etc., present in the gas is a very small proportion of the total (often not more than 1 per cent.). The total amount of benzol recoverable may be estimated by utilising a creosote absorption system on a small scale. Thus immediately before entering the benzol scrubbers a measured volume of the gas should be passed through a train of wash bottles, sufficient gas being dealt with to give a quantity of benzol large enough to be able to establish its identity by a subsequent distillation test. On an average about 50 cub. ft. of gas will be required. The train of washing apparatus consists of a preliminary bottle containing dilute sulphuric acid to remove ammonia, followed by four wash bottles each containing prepared creosote, glass beads also being introduced to increase the contact surface. The creosote used should be quite fluid, free from naphthalene, and should be previously distilled up to 200° C., rejecting the distillate. The rate of flow of the gas should be kept as uniform as possible, divided over a period of, say, forty-eight hours. The total amount of creosote used would be about 2 litres, and should be changed about every eight hours, approximately 100, 100, 65, and 65 c.c. being put in the respective bottles each time. We thus obtain 2 litres of a benzolized oil, and for a complete test this must be subjected to a distillation to 200° C. (in several portions if the apparatus is not large enough). The distillates are totalled and can now be treated in one flask, distilling up to 150° C. The product coming over up to this temperature is carefully measured, and then subjected to the usual crude benzol test, the volume then being corrected to its equivalent of benzol, testing 65 per cent. at 120° C. The above process is somewhat tedious, and is only used occasionally to test the efficiency of the plant. For comparative purposes much smaller quantities are used, and though not as reliable, serve to indicate any serious drop in efficiency.

Tests may be conducted on the gases after the benzol scrubbers, but here the difficulty is emphasised owing to the still smaller proportion of benzol. In this case the amount of benzol recovered is too small to be reliably identified, and the test under good conditions can only be considered comparative

of daily results at any one plant, and consequently all the details of working, such as rate of flow of gas, nature and quantity of absorbing oil, method and rate of distillation, etc., should be kept on a uniform system.

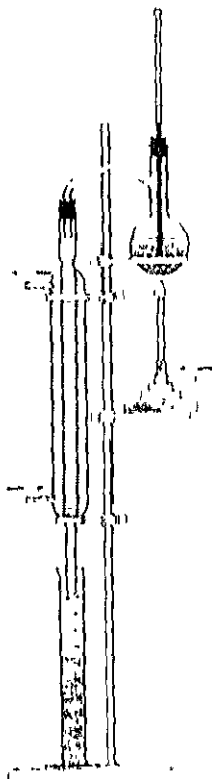


FIG. 49. Benzol Distilling Apparatus.

Crude benzol is generally tested in an ordinary 8 oz. retort, the bulb of the thermometer being fixed about $\frac{1}{8}$ of an inch from the bottom. A convenient arrangement of distilling flask and condenser, etc., giving similar results as used by the authors, is shown in Fig. 49. Occasionally it is desired to ascertain the probable yield of semi-pure and pure products from crude benzol. Whilst laboratory methods usually deal with quantities rather small for comparison with results on a manufacturing scale, a general idea of the yield and nature

of the products may be obtained. The authors have found the following method most convenient for that purpose.

The crude benzol is distilled in a flask with a side outlet up to 200°C , and the residue measured and classed as wash oil, naphthalene, etc. The distillate is then washed with strong sulphuric acid three times, water twice, caustic soda once, and finally with water twice. After separation of water the washed product is dried by suspending a little calcium chloride, and

removing the same when the benzol clears. The washed and dried product is then transferred to a distillation flask, in this case fitted with an adapter consisting of a glass tube about 8 in. long, $\frac{3}{4}$ of an in. in diameter, and fitted with a simple bulb about $1\frac{1}{2}$ in. diameter. Near the top of this adapter an outlet tube is fitted and connected to a suitable condenser, fixed vertically for convenience. A thermometer is introduced with the bulb half an inch below the side outlet. With an adapter of this description a slight fractionation of the vapour occurs, giving products which correspond fairly satisfactorily with yields on a works scale. The distillates at 100°, 120°, 160° are collected, measured, and classed as 90 per cent benzol, 90 per cent. toluol and solvent naphtha respectively, the residue in the flask being considered as heavy naphtha. Details of an actual test are given below:—400 c.c. crude benzol (testing 65 per cent. at 120° C.) distilled in two lots to 200° C.

Distillate = 348 c.c.

Residue = 52 c.c. = Creosote, etc. = 13 per cent.

348 c.c. washed with acid, soda, etc., gave 290 c.c. washed product. Loss on washing, 58 c.c., or 14.5 per cent. on the original sample.

290 c.c. distilled in two lots gave:—

Up to 100° C.	-	216 c.c., or 51 per cent.	on original sample.
100° to 120° C.	-	12 c.c., or 10.5	„ „ „
120° to 160° C.	-	24 c.c., or 6.0	„ „ „
Residue	-	8 c.c., or 2.0	„ „ „

The final analysis thus reads:—

90 per cent. benzol	-	-	-	51.0 per cent.
90 „ toluol	-	-	-	10.5 „
Solvent naphtha	-	-	-	6.0 „
Heavy naphtha	-	-	-	2.0 „
Creosote, etc.	-	-	-	13.0 „
Loss on washing	-	-	-	14.5 „

It is an advantage to carry out a few distillation tests to secure sufficient of each fraction to test in comparison with well recognised products. Thus the several curves may be

compared with those shown in Fig. 50, which represent distillation curves of washed 90 per cent. benzol, 50 per cent. benzol, 90 per cent. toluol, and solvent naphtha. The products from the quantitative tests should agree fairly well with these curves.

To estimate the proportion of pure product, a more

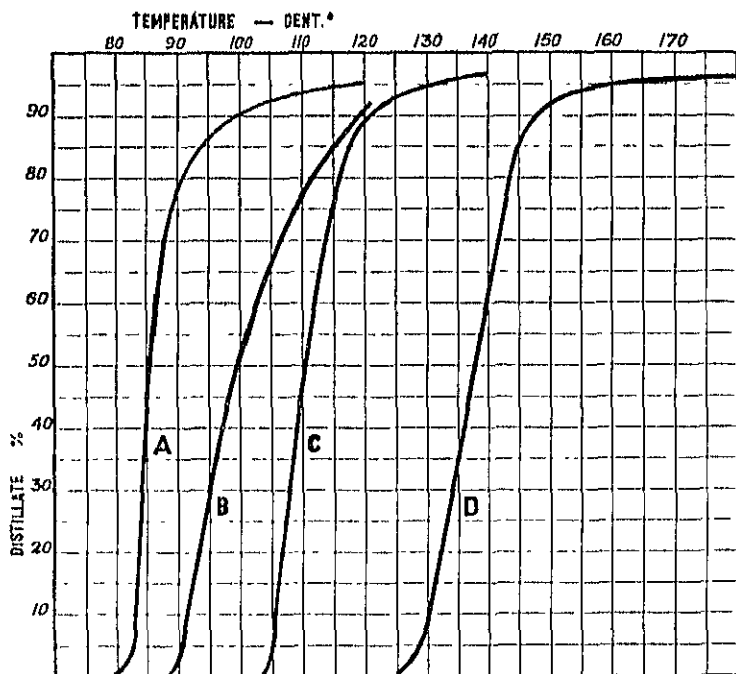


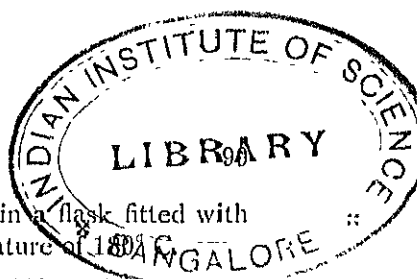
FIG. 50. - Distillation Curves of Benzol, etc.

elaborate procedure is necessary, and after several trials with methods advocated by various observers, the writer has found an adaptation of the scheme described by Edwards¹ well suited for this purpose. Details of a test carried out by the writer on these principles are given below —

100 c.c. crude benzol (from the same store tank as the

¹ "The Estimation of Benzene and Toluene in Commercial Mixtures,"
A. Edwards, *Journ. of Soc. Chem. Ind.*, 35, 10, 587.

BENZOL



previous test) were distilled in two lots in a flask fitted with a 12 bulb Young column up to a temperature of 180°C .

Distillate	-	-	-	340 c.c. (A).
Residue	-	-	-	60 c.c. (B).

(A) Redistilled in same apparatus to 145°C .

Distillate	-	-	-	314 c.c. (C).
Residue	-	-	-	26 c.c. (D).

(C) 1. Washed three times with sulphuric acid (1.81), using 5 per cent. by volume each time, and shaking for two, five, and five minutes respectively.

2. Gently washed with water.

3. Washed with caustic soda and water.

4. Dried with calcium chloride.

(E) Result—290 c.c. washed and dried product.

Loss—24 c.c., or 6 per cent. on original sample.

(E) Fractionated in same apparatus :—

1. Up to 85°C .	-	-	-	128 c.c.
2. 85° to 96°	-	-	-	97 c.c.
3. 96° to 110.7°	-	-	-	26 c.c.
4. 110.7° to 125°	-	-	-	26 c.c.
5. Residue	-	-	-	13 c.c.

1. Refractionated to 80.2° gave 33 c.c. "First runnings," 95 c.c. to No. 2.

3. Refractionated to 110.7° gave 15 c.c. to No. 2, 11 c.c. to No. 5.

4. Refractionated to 110.7° gave 14 c.c. to No. 2, 12 c.c. to No. 5.

No. 2 and No. 5 not refractionated, but augmented by the above distillates and residues, giving—

33 c.c. - First runnings.

221 c.c.—No. 2, consisting of a mixture of benzene and toluene.

36 c.c.—No. 5, consisting of a mixture of toluene and xylene

The proportion of benzene and toluene in No. 2 is found by ascertaining the boiling point of the mixture in a boiling point apparatus fitted with a reflux condenser as shown in the original paper. This will range between 80.2° and 110.7°C , the boiling points of benzene and toluene respectively. From the boiling point of the No. 2 fraction, which was found to be 82.9°C , the proportions were read off from

a curve constructed from data in the paper, showing 84 per cent. benzene and 16 per cent. toluene, or calculated on the volume of the mixture (221 c.c.), a proportion of 185.6 c.c. benzene and 35.4 c.c. toluene. On similar lines No. 5 gave 26.5 c.c. toluene and 9.5 c.c. xylene. These two results, totalled, gave the following analysis:—

33 c.c.	First runnings, or 8.2 per cent. on original.
185.6 c.c.	Benzene, or 46.4 per cent. on original.
61.9 c.c.	Toluene, or 15.5 " "
9.5 c.c.	Xylene, or 2.4 " "

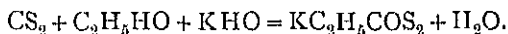
The two residues B and D were totalled and distilled to 190° C., giving 31 c.c. naphthas, or 8.5 per cent., and 52 c.c. creosote, or 13.0 per cent., on original sample. The final analysis would thus be given as:—

First runnings	-	-	8.2 per cent.
Benzene	-	-	46.4 "
Toluene	-	-	15.5 "
Xylene	-	-	2.4 "
Solvent and heavy naphtha	-	-	8.5 "
Creosote oil	-	-	13.0 "
Loss on washing	-	-	6.0 "

It is often of importance to know the amount of carbon disulphide in benzol, especially if the latter is for nitration purposes. Probably the best method depends upon the formation of potassium xanthate by the interaction of the carbon disulphide and alcoholic potassium hydroxide. The xanthate may then be dealt with in several ways—

- (a) Titration, after solution in water and acidifying, with a standard solution of copper sulphate.
- (b) Addition of an excess of copper sulphate to an acidified aqueous solution of the xanthate, filtration, washing, and ignition of the precipitated xanthate to cupric oxide, which is weighed.
- (c) The aqueous solution treated with potassium hydroxide and bromine, by which means all the sulphur is oxidised to sulphate. This is precipitated in the form of barium sulphate by adding an excess of barium chloride to the acidified

solution. The BaSO_4 is filtered off, washed, ignited, and weighed as such. The reaction which takes place in the formation of the xanthate is as follows—



The alcoholic potassium hydroxide is made by dissolving 11 gm. of potassium hydroxide in 90 gm. of absolute alcohol. The standard solution of copper sulphate contains 12.475 gm. of the crystals dissolved in distilled water and made up to a volume of 1 litre.

1 c.c. of this solution is equivalent to .0076 gm. of carbon disulphide.

In making a test, 50 gm. of benzol are mixed with an equal weight of the alcoholic potassium hydroxide. The mixture is allowed to react for several hours with occasional shaking. The xanthate will separate in the form of yellow needles. These are dissolved out by shaking with water in a separating funnel several times, the aqueous extracts thus obtained being used for the copper titration, after being acidified with acetic acid.

If the gravimetric method (*b*) is adopted the aqueous extract of the xanthate is acidified with acetic acid, and an excess of copper sulphate added, the precipitated cupric xanthate, $\text{Cu}_2\text{H}_6(\text{CO})\text{S}_2$, being filtered off, etc., and weighed finally as cupric oxide, with the usual precautions.

The amount of carbon disulphide in 90 per cent. benzol averages from 1 to 2 per cent

Since other sulphur compounds are usually present in benzol, in addition to carbon disulphide, it is sometimes desirable to determine the total sulphur. In doing this the general principle is to burn a weighed quantity of the benzol in a small lamp, with an ample air supply. In burning, the sulphur compounds become converted into sulphur dioxide. This may be dealt with in several ways:—

- (a) Absorption in acid or in alkaline solutions of bromine, whereby the sulphur is further oxidised to sulphate, and is finally weighed as barium sulphate, after precipitation with an excess of barium chloride.

(b) Absorption in an ammoniacal atmosphere, with final oxidation to sulphate either by bromine water or a little hydrogen peroxide, also finally weighing as barium sulphate. The ammonia may be supplied by placing a few pieces of ammonium carbonate round the burner.

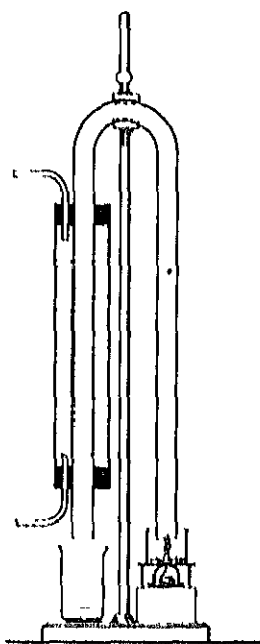


FIG. 51 Estimation of Total Sulphur in Benzol, etc

In any case, the combustion of the oil must not be too rapid. A very small flame is required, and the process usually extends over several hours. A convenient type of apparatus for this purpose is shown in Fig. 51. In testing for thiophene (C_4H_4S), 2 c.c. benzol are agitated with 20 c.c. of a mercurial solution, consisting of 1 gm. HgO dissolved in 1 c.c. concentrated sulphuric acid, and diluted to 20 c.c.

The mixture is then heated on a boiling water bath for one hour. It is then cooled and filtered, the precipitate washed with hot water, dried at 110 to $115^\circ C$, and weighed.

Weight $\times 0.758$ Thiophene.

CHAPTER IX

SURPLUS POWER, ETC.

A CONSIDERABLE amount of energy may be derived from a modern coke plant, and even after deducting the requirements of the plant itself in the form of power to drive the disintegrators, rams, charges, exhausters, etc., and in the form of steam for the sulphate plant, benzol plant, etc., there is, as a rule, a surplus for external purposes. According to the type of oven, this energy may be derived from waste heat, surplus gas, or from a combination of the two. In the case of a waste heat oven the bulk of the power must necessarily be derived from steam, a relatively small proportion of the power being obtained from surplus gas. In utilising the waste heat the efficiency of the (*a*) boiler plant and (*b*) power plant is in many cases influenced by factors independent of the working of the coke plant. The type of boiler, prime mover, quality of water, etc., exercise effects which may be looked upon as a constant. Considerable improvement has been effected in recent years by replacing compound engines and inefficient boilers with steam turbines, multitubular boilers, water softening plants, etc., and still more recently the transmission of heat from the spent products of combustion to the water has received considerable attention with beneficial results. Whereas at one time a regenerative oven producing power by means of internal combustion engines had an advantage over a waste heat plant using steam for this purpose, developments in the generation and utilisation of steam have somewhat levelled up the comparison, and there is little to choose between the two schemes at the present moment. Seeing that an appreciable amount of steam is required in the by-product section, many designers prefer to use steam also for power production to secure uniform working of the plant in general, the surplus gas being burnt

under the boilers to augment the effect of the waste heat. In many cases gas has been burnt for this purpose without any serious regard for efficiency, and the method of introducing spare gas into boilers through open pipes or badly designed Bunsen burners is to be deprecated from the standpoint of national economy. In the majority of cases the waste heat is conducted to the boiler tubes by special brick-lined connections, preferably in the form of bends adapted for easy removal for cleaning purposes and repairs. Fig. 52 is an illustration of a suitable type for Lancashire boilers (W. C. Holmes & Co., Huddersfield). Bunsen burners

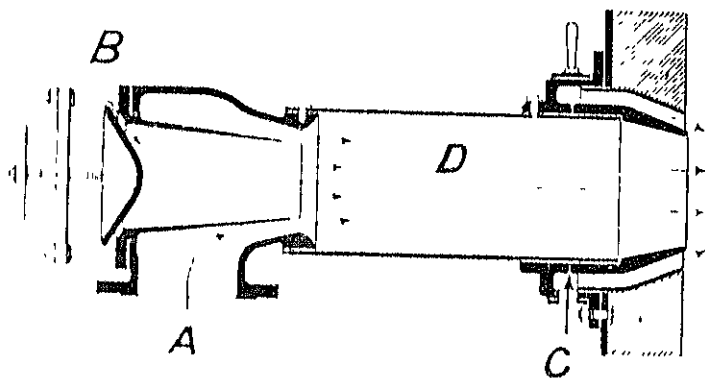


Fig. 53. Burner for Coke Oven Gas. (Ferbeck type.)

adapted for use with coke oven gas may be fitted to these tubes as shown. A considerable volume of air is required in these burners, approximately five times the volume of gas, and it is usually admitted in two stages, primary air near the gas inlet, and secondary air at the outlet of the mixing tube. Two types of burners for coke oven gas are shown. Fig. 53, Ferbeck burner (Coke Oven Machinery Co., Evesham), and Fig. 54 (Altenheim & Wilson, Mayport). In each case gas is admitted at A, primary air at B, the two passing through the mixing chamber D, secondary air being supplied at C. Variations in the pressure of gas affect the proportions of gas and air considerably, occasionally giving rise to back firing or extinguishing of the flame. In the latter case there is risk of explosion in the boiler flues unless,

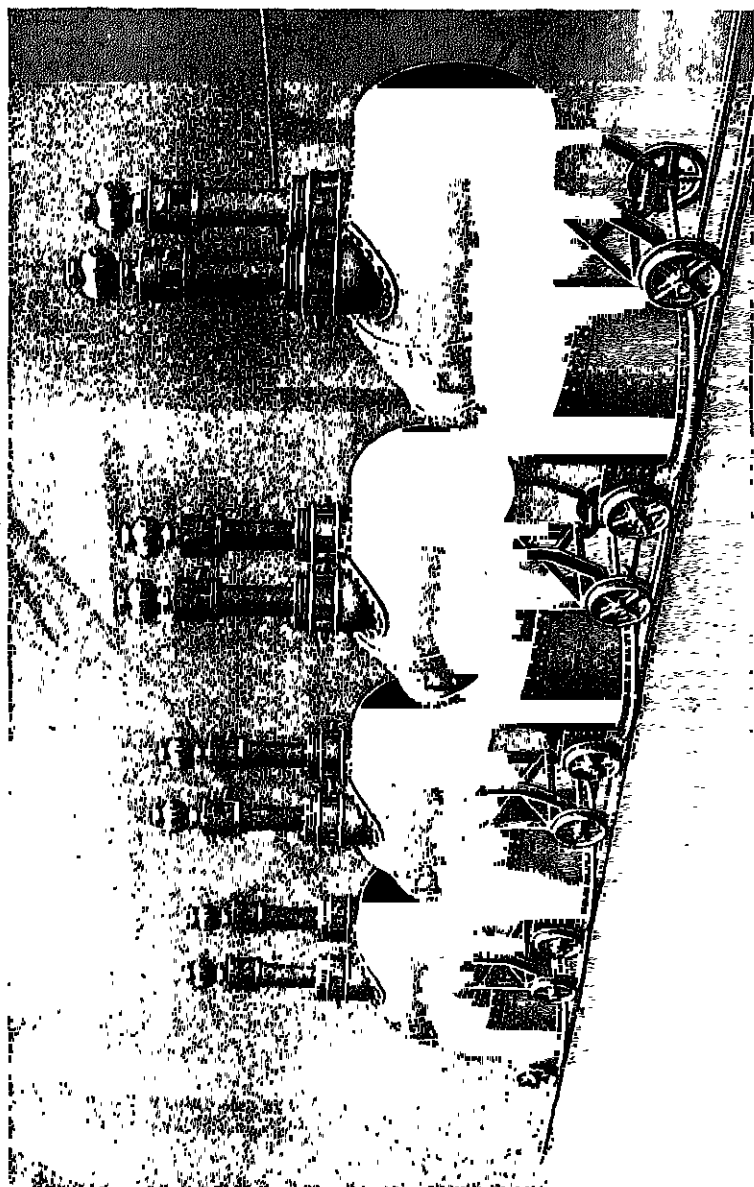


FIG. 12.—CONNECTIONS FOR WASH HEAT BOILERS (W. C. Holmes & Co.)

Fig. 100 of ample surface adapted to become incandescent. The combustible mixture sweeps over the incandescent surface, and, by contact therewith, burns by surface combustion at a highly accelerated rate. The heat is rapidly transmitted by radiation, and owing to this rapidity of combustion and transmission the tubes are much shorter than in ordinary boiler practice. To cope with the high rate of evaporation, the exhauster is used to create a suction up to 16 in. of water. At a ten-hour steam trial with

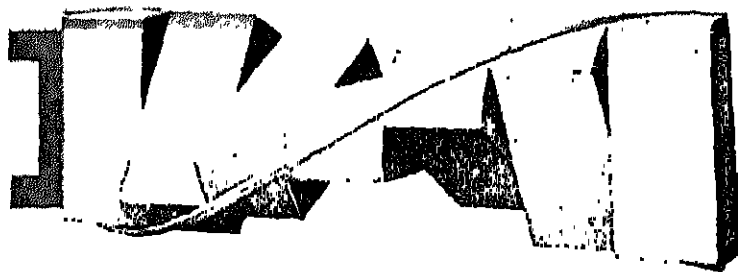


FIG. 50. Refractory Filling for Tubes of Bonecourt Boiler.

a Bonecourt boiler and feed-water heater the following results are quoted:—¹

Caloric value of gas	510.5 B.Th U. (net) per cub. ft.
Gas burnt (N.T.P.)	101,853 cub. ft.
Water evaporated, from and at 212° F.	19,824 lbs.
Evaporation per square foot of heating surface	14.4 lbs. per hour
Temperature of products leaving boiler	386° F.; 196° C.
Temperature of products leaving feed-water heater	202° F.; 94.6° C.
EFFICIENCY	92.7 per cent

The waste heat boiler of the same firm is designed on similar lines, except that no burners are necessary, and the suction required is much less (about 2 in. water gauge above the requirements of the ovens). In dealing with a regenerative

¹ "Howard Lectures on Surface Combustion," Prof. Bone, Royal Soc. of Arts, 1914.

type of coke oven an entirely different set of circumstances arises. First the absence of available waste heat renders the use of steam engines as prime movers optional, giving a choice of three systems of utilising the surplus gas, as:—

- (a) Lighting.
- (b) Power from internal combustion engines.
- (c) Power from steam.

With regard to the first method, the composition of the

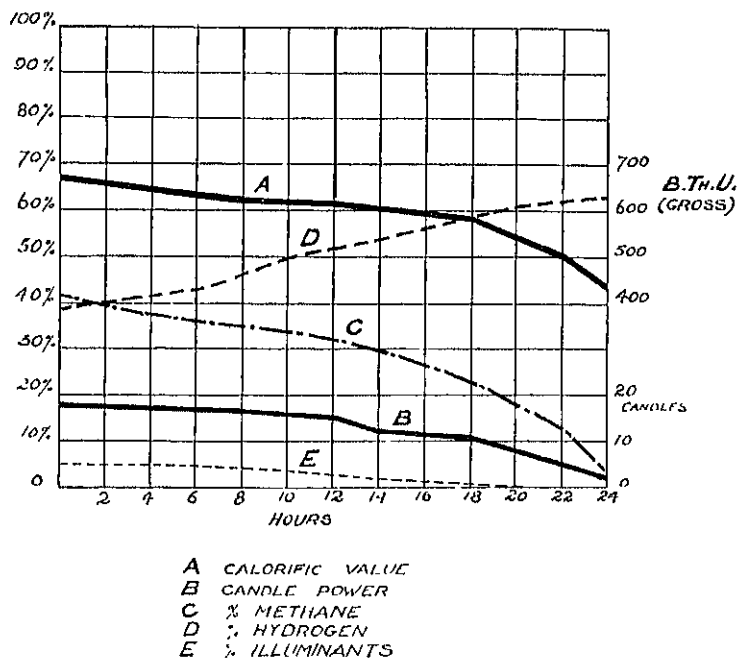


FIG. 57.—Variation in Composition of Coke Oven Gas.

gas from any individual oven varies considerably from the beginning to the end of a charge. Fig. 57 shows the gradual change in composition, and it will be seen that the gas from the first half of the coking period is much richer than that from the second half, and by taking the rich gas through separate mains and by-product plant there would be little difficulty in supplying gas to meet the required standard, but in the writer's opinion a modern coke plant in a reasonable

state of repair could produce an average gas suitable for the conditions of gas lighting, likely to obtain in the future. In addition, the removal of benzol brings about an appreciable diminution in the content of carbon bisulphide in the gas. Since the great majority of towns in this country have already good gas plants, the field for lighting with coke oven gas appears to be confined to replacing a portion only of the gas now being made at any individual gas works, and the writer suggests that the purification and distribution of the gas should be left to the gas works as part of their general scheme in that respect. Some coke oven erecting firms (Koppers, Simon Carves, Otto, etc.) have patented means whereby the ovens may be heated by producer gas if desired. In this case the whole of the coke oven gas is available for lighting and other purposes, whilst the producer gas may be generated from an inferior fuel, including as such the coke breeze of the plant. The design of the flues is modified to admit a greater proportion of gas to air (1 to 1 as against 1 to 5 with coke oven gas), and means are provided for preheating the producer gas in the regenerative system as well as the air.

In a few instances in connection with ovens attached to iron and steel plants, blast furnace gas has been introduced into the oven flues with success, increasing the amount of coke oven gas available for use in the steel works, smelting and heating furnaces, etc. If an outlet for surplus gas for lighting or heating purposes is not available, then the gas must be used for the production of power by means of gas or steam engines. In the latter case, unless steam turbines and boilers of the Honecourt type are used, the writer sees no reason why the additional expense of regenerators should be incurred. Engineers in this country have had much more extended experience in steam plants than in gas engine plants, whilst the reverse is the case on the Continent. There the large gas engine using coke oven gas is more popular, and the special difficulties in dealing with a rich gas, with a high hydrogen content have been overcome. In general, the compression pressure has been reduced, often to below 100 lbs. per sq. in., and in many cases the gas is diluted with blast furnace gas, producer gas, or even exhaust gases. More recently the heat of the exhaust has been turned to good effect by passing it

through a multitubular boiler coupled to a steam turbine, the boiler acting as an effective silencer as well as materially increasing the over-all efficiency of the plant. A gas-holder capable of carrying over possible short stoppages on the coke plant is an advantage, and a purifying system, whilst removing any likelihood of corrosion in the valves, etc., also secures the sulphur in a form capable of being readily converted to a valuable commodity, sulphuric acid.

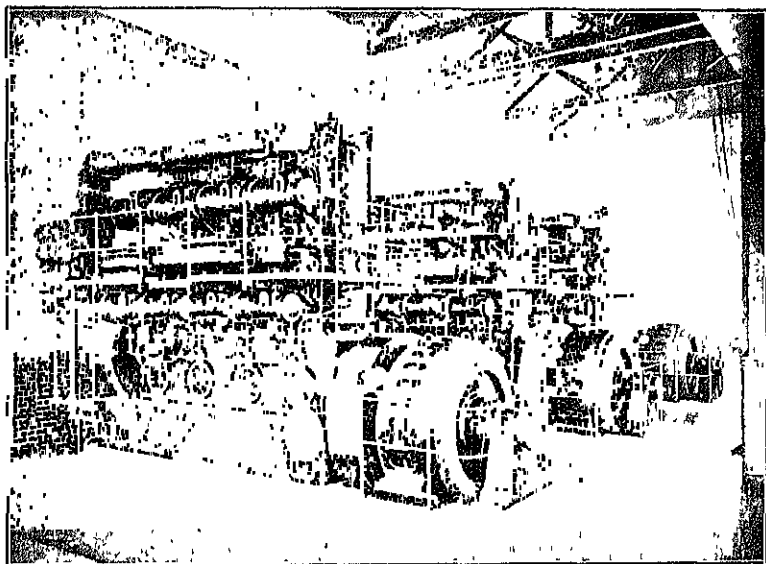


FIG. 58. —Gas Engines on Coke Oven Gas (National Gas Engine Co.)

Fig. 58 shows an example of a British type of gas engine working on coke oven gas (National Gas Engine Co., Ashton-under-Lyne). This engine is of the vertical totally enclosed type, having two up to six cranks in each set according to the size of the engine, the cylinders being arranged in tandem fashion and operating on the four cycle or "Otto" principle. Thus a 1,000 B.H.P. set would have four cranks, with a stroke of 24 in. and working at 200 revolutions per minute. By utilising a vertical type of engine a considerable economy in floor space is effected, whilst the arrangement of multiple cylinders brings about an exceptionally even turning move-

ment. The gas should be supplied to the engine under pressure (from 1 to 3 in. of water above atmosphere). It should be free from dust, but a "dusty" condition is not likely to arise in coking practice. It should be practically free from tar, and should not contain more than 0.2 gm. sulphur per cubic metre. The quality of the cooling water and of the oil for lubrication is also an important factor. Details of a test on a National gas engine working on coke oven gas are given below :—

	Full Load.	Half Load.
Gas temperature - - -	18.2° C.	19.3° C.
Gas pressure - - - -	3.125 in.	4.125 in.
Gas used per B.H.P. hour -	23 cub. ft.	21.6 cub. ft.
Calorific power of gas (gross) -	468	525
Calorific power of gas (net) -	420	478
B.Th.U. per B.H.P. hour	9,664	11,770
H.P. thermal efficiency - -	26.4	21.6
Water used per hour -	2,850 galls.	3,100 galls.
Total B.H.P. -	530	286

CHAPTER X

GAS ANALYSIS, PYROMETRY, ETC.

IN the scientific control of a coke plant the composition of the gas from the ovens and of the waste gases, say, at the chimney, should be periodically ascertained, and for this purpose the authors have found the apparatus designed by Mr Stead to be very suitable (Fig. 59).

The reservoir on the left of the diagram contains mercury, and this is connected with the eudiometer and levelling tube by means of the U-shaped joint. The eudiometer or measuring tube is graduated in millimetres, and has platinum wires fused through the upper portion for the explosion of gaseous mixtures. The tube of the eudiometer is drawn out at the top to a bore of about 3 mm., and is connected to a three-armed capillary tube, to which three absorption vessels may be attached (only one is shown in the figure). The capillary tube is also extended to the right, and through this the sample of gas is taken into the eudiometer. It will be seen that by raising the mercury reservoir, by means of a cord holding a counterweight and passing over pulleys, the mercury will flow into the eudiometer, and, the tap being opened, any gas or air in the tube will be completely expelled. The gas sample, or bottle containing the sample of gas, may now be attached to the end of the capillary tube, and by lowering the mercury reservoir any desired volume may be drawn into the eudiometer for analysis, and the tap shut off. By means of the levelling tube the pressure is kept constant, since it is open to the atmosphere; and also, by means of a water jacket round the eudiometer (not shown in the figure), the temperature is constant, thus avoiding corrections otherwise necessary. The gas, after measurement, is passed into the various tubes connected to the three-armed piece containing various absorbents. It will be readily seen

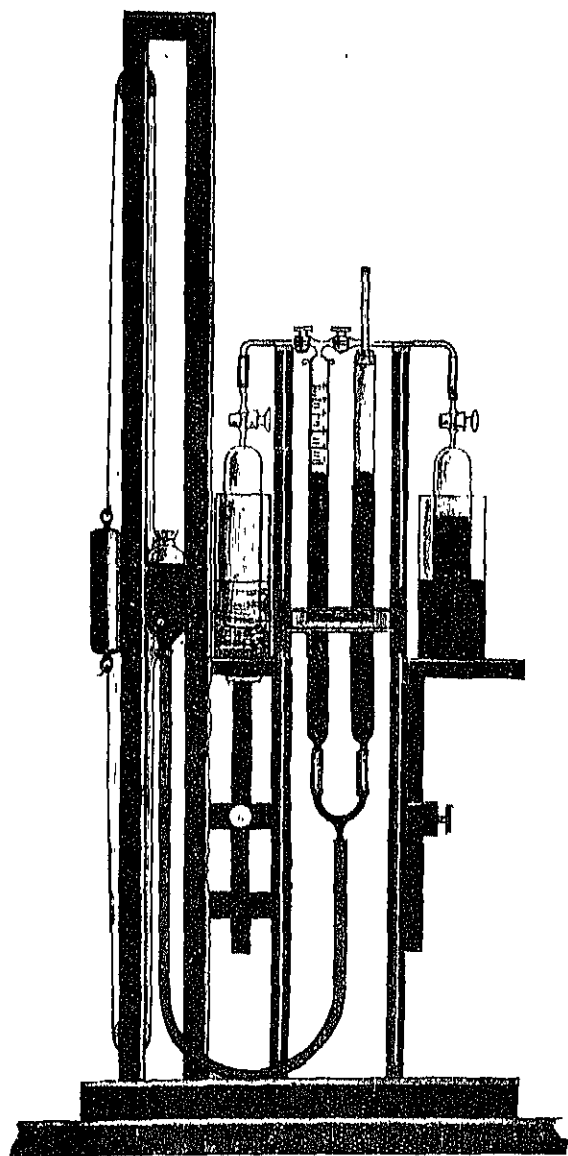


FIG. 59.- STEAD'S APPARATUS FOR GAS ANALYSIS.

that the gases may be transferred from one absorbing vessel back to the eudiometer for measurement, and then into other absorbents as desired, by manipulating the mercury reservoir. In an analysis of oven gas the following would be the procedure:—

Take a measured quantity of gas, say about 200 c.c., into the eudiometer, measuring carefully with the mercury at the same level in the eudiometer and levelling tube; then pass over into one of the absorbing vessels containing a solution of potassium hydrate, leaving it several minutes in contact; then pass back into the eudiometer for measurement. The diminution in volume is due to the absorption of carbon dioxide. The gas is then passed into fuming sulphuric acid or bromine solution, which absorb olefines and benzenes, but before final measurement any vapours of sulphur trioxide or bromine must be got rid of by passing over into the potash vessel. The next absorbent used is an alkaline solution of pyrogallie acid (pyrogallate of soda), which takes up oxygen, and finally cuprous chloride is used to absorb the carbonic oxide. An extra absorbing vessel can readily be attached to one of the three arms, or detached to be replaced by any special absorbent. The remaining gases now consist of marsh gas or methane, hydrogen, and nitrogen. To determine the two former, they are mixed with a certain volume of air and an electric spark passed across the platinum wires in the eudiometer. By this means the methane becomes converted into carbon dioxide and water, and the hydrogen becomes water. There is a contraction in volume after explosion, and this is carefully measured, and then the mixture is passed into the potassium hydrate to absorb the carbon dioxide, which is measured by the diminution in volume after several minutes' contact. It is advisable to take about 20 to 25 c.c. of gas for explosion after removal of carbonic oxide, etc., by absorbents, and dilute with about 200 c.c. of air free from carbon dioxide. If oxygen be used the explosion would be violent enough to burst the eudiometer. The methane, when exploded with air, forms its own volume of carbon dioxide, hence the last absorption represents the volume of methane present. But in exploding, methane requires twice

its volume of oxygen. Therefore by taking twice the volume of carbon dioxide formed from the total contraction, the difference is the contraction due to the explosion of the hydrogen, and two-thirds of this contraction is due to hydrogen.

The nitrogen is always estimated by difference. The calorific value of coke oven gas may be calculated from the results of the above analysis on the basis shown in the table on p. 58, Vol. I., with results fairly concordant with those arrived at by experiment. At the same time the tendency in statutory conditions appears to be inclined towards the adoption of a calorific standard, and an instrument for determining the calorific power of a gas is almost a necessity on a well-conducted coke plant. Modern instruments are usually of the "flow" type in which a measured quantity of gas is burnt, and the heat transferred to a supply of water flowing through the instrument at a uniform rate. From the difference in the temperatures of the inlet and outlet water the calorific power is estimated.

Fig. 60 shows the principle of the Junker calorimeter. The gas, after passing a governor to ensure a steady pressure, is burnt in the Bunsen burner K, and the heated products of combustion rise in the chamber A and descend by way of a series of vertical tubes B surrounded by the water flowing through the instrument. The rate of flow of the water is regulated by the quadrant tap E, and a constant head is secured by the overflow arrangement at D. Condensation products may be collected at H and measured. The apparatus is enclosed in an air jacket G to minimise the effects of radiation. The damper C assists considerably in bringing down the temperature of the products of combustion to a point only a few degrees above atmospheric temperature. The thermometers shown give the temperature of the water at the inlet and outlet, but in later types these thermometers are brought to one level to assist in the reading. The gas is ignited, and after allowing the instrument some time to ensure a fairly uniform flow of gas and water, and having adjusted the gas flow to a rate of about 6 or 7 cub. ft. per hour, the reading of the meter is taken, and simultaneously the water leaving the calorimeter is directed to a measuring jar. After

burning the required quantity of gas (say about .3 cub. ft.) the final reading of the meter is taken, and by means of a swivel bend the water is diverted from the measuring jar.

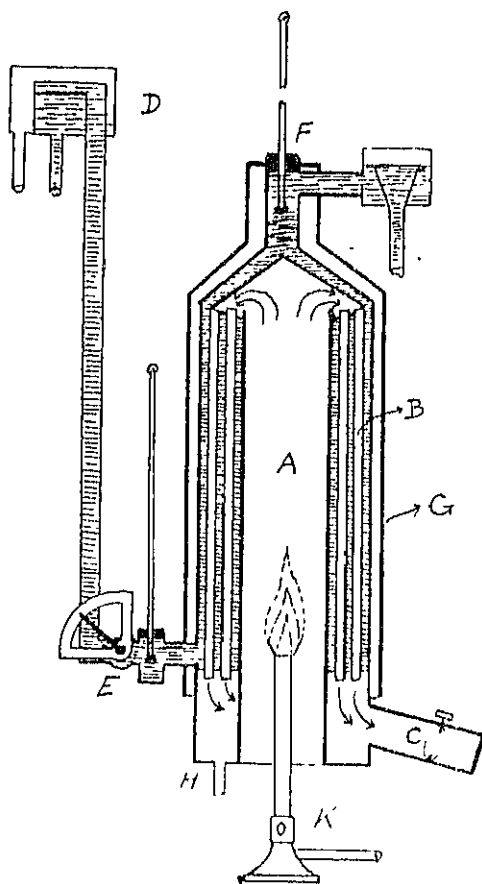


FIG. 60.—Junker's Gas Calorimeter, in Section

During the burning of the gas periodical readings of the water thermometers are taken, and the average rise in temperature noted. Then from these data we may calculate the gross calorific value of the gas. If we wish to ascertain the net calorific value the water of condensation must be collected. It is found more convenient to use the metric system in these

experiments, and the result may afterwards be readily converted from calories per cubic metre, etc., to B.Th.U. per cubic foot.

An example of an actual test is given below :—

Volume of gas burnt	-	-	-	6,500 c.c.
Temperature of gas	-	-	-	22° C.
Pressure of gas	-	-	-	780 mm.

Corrected volume of gas :-

$$6500 \times \frac{780}{760} \times \frac{273}{273 + 22} = 6170 \text{ c.c. or } \cdot 218 \text{ cub. ft.}$$

Water passed through calorimeter	-	-	-	2,770 c.c.
Water of condensation collected	-	-	-	3 c.c.
Temperature of water at inlet	-	-	-	19.45° C.
Temperature of water at outlet (average)	-	-	-	29.20° C.
Rise in temperature of water	-	-	-	9.75° C.

The total heat produced is .

$$2770 \times 9.75 = 27.0075 \text{ cal.} \quad \text{Less heat represented by the } 3 \text{ c.c. of water condensed } = 3 \times .6 = 1.8 \text{ cal.}$$

(.6 cal. latent heat of steam + sensible heat in cooling from 100° C. to outlet temperature of gas per c.c. of water.)

The gross calorific value is - - - - - $27.0075 \div \cdot 218$ or 123.9.

The net calorific value is - - - - - $(27.0075 - 1.8) \div \cdot 218$ or 115.6.

Calories per cubic feet. To convert to B.Th.U. multiply by 3.96, giving

Gross calorific value	-	-	-	490.5 B.Th.U. per cub. ft.
Net calorific value	-	-	-	457.7 B.Th.U. per cub. ft.

In the Boys calorimeter a smaller volume of water is in the apparatus at any particular moment, the water flowing through two spiral copper tubes gilled with wire to assist in the abstraction of heat from the test flame. Two luminous flames from special jets are used. The instrument is very compact and convenient, the thermometers being at one level and the parts being easily accessible for cleaning, etc. Fig. 61 shows a recent type of recording calorimeter (Simmons's Total Heat Calorimeter, Alexander Wright & Co., Westminster). In view of the probable trend of future Parliamentary conditions the instrument is designed to give

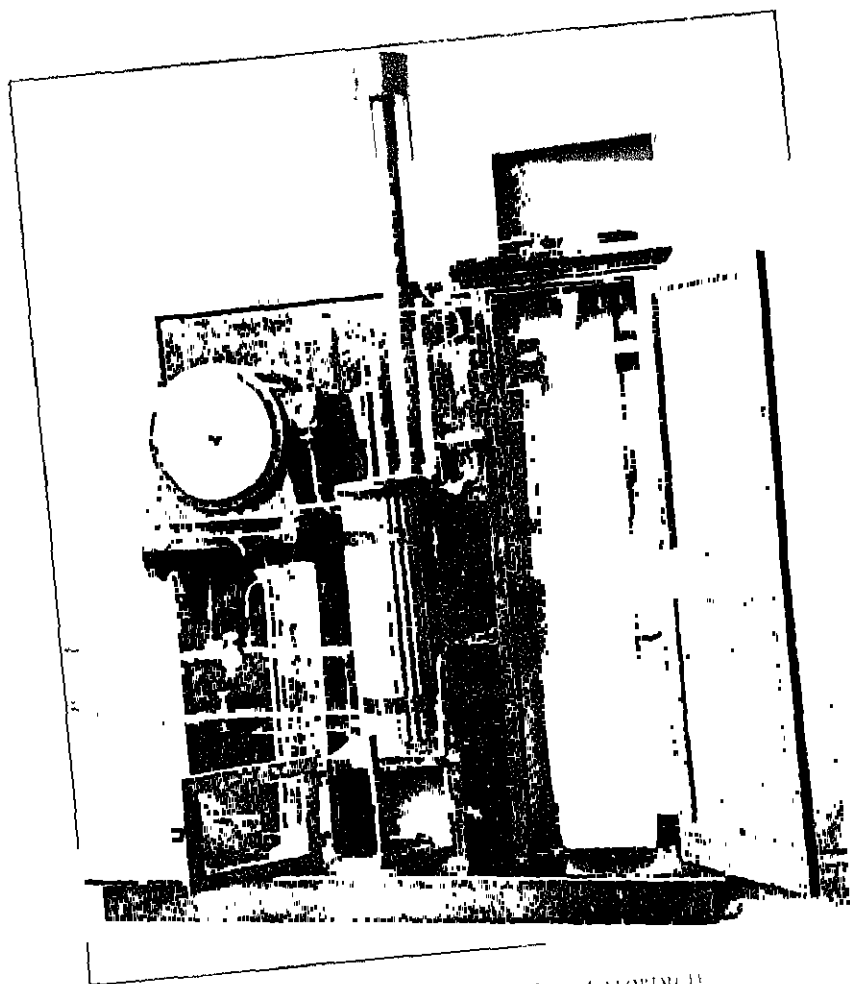
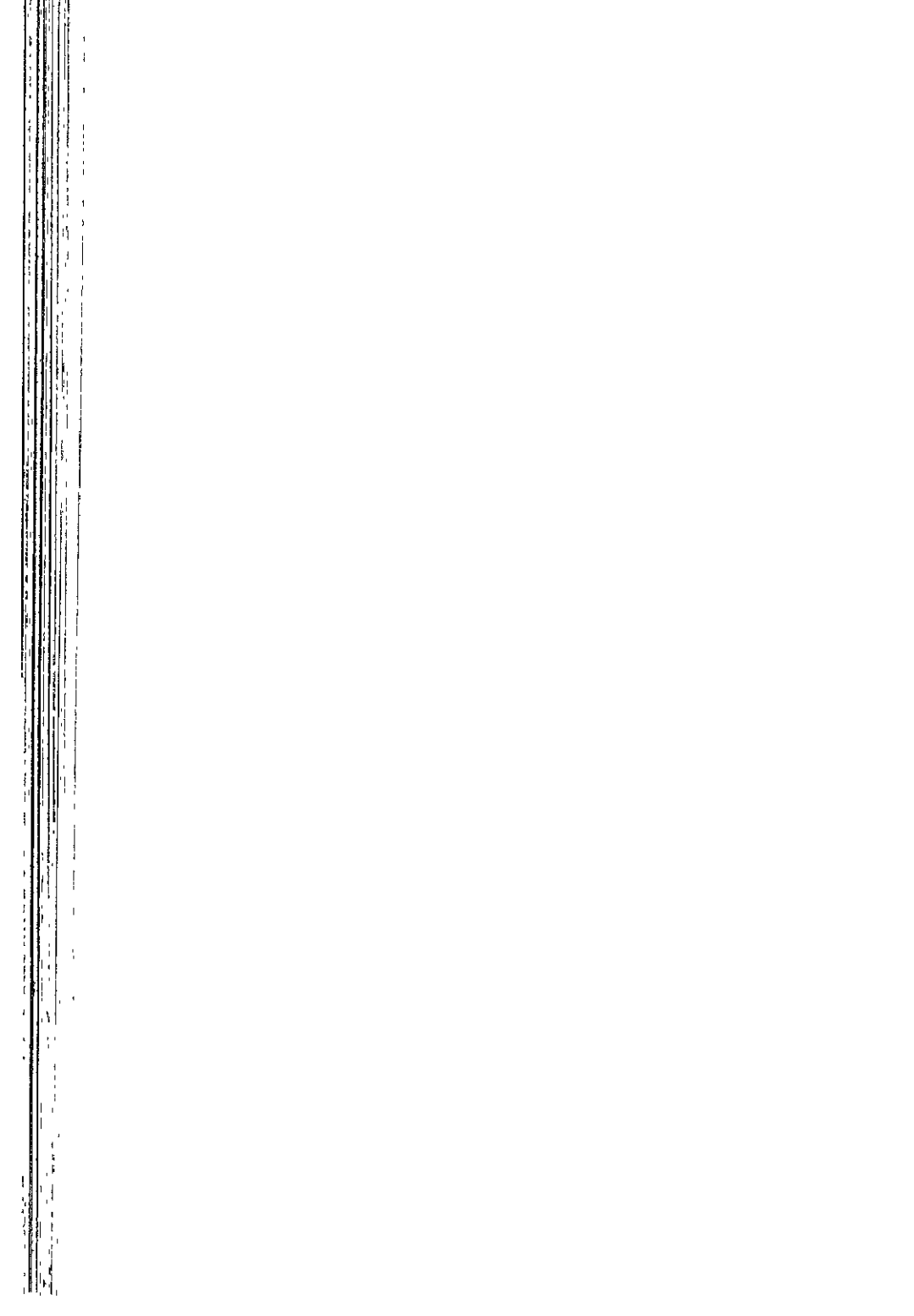


FIG. 61.—SUMMERS'S TOTAL HEAT CALORIMETER
(Alexander Wright & Co.)

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a continuous record of the total heat value in gross heat units, recorded at normal temperature and pressure, and requiring no correction of any kind. An individual test can be made independent of the record, and means are provided for ensuring that the air supplied to the burner is always saturated at cold water temperature, and by means of a gravity governor variations in specific gravity are automatically neutralised.

The control of the temperature at various parts of a coke plant is an important factor. For the measurement of temperatures in the by-product section generally the mercury thermometer is a suitable instrument, but for the temperatures obtaining in the interior of the coke oven or coke oven flues, boiler flues, base of chimney, etc., other means are adopted for ascertaining the temperature. One very ready and convenient method is by means of Séger's cones or pyroscopes. These are made of material consisting of silicates of varying composition moulded into the form of tetrahedra or triangular pyramids. By varying the proportions of the ingredients used in making the cones, it is possible to alter the temperature at which they fuse. There are some fifty-eight different mixtures having melting points ranging from 590° C. to $1,850^{\circ}$ C. By subjecting a few of these to the temperature the degree of which it is desired to estimate, and noting the effect upon them, it is easy to determine, quite accurately for all practical purposes, what the temperature is. The Watkin's heat recorders are based on somewhat similar principles. They consist of blocks of refractory material with circular recesses sunk in the top face. In these recesses are placed small pellets of fusible materials of definite composition and melting point, the latter having been determined by means of a standard electrical pyrometer.

Watkin's heat recorders may be used by inserting one at the end of an iron tube, placing the tube inside the oven flue, etc., through an inspection hole, and carefully sealing up with clay the protruding ends of the tube, as also the space round the outside of the tube at the inspection hole. After a full five minutes the tube may be withdrawn, the condition of the recorder observed, and the temperature determined accordingly. In the majority of cases electrical or radiation

pyrometers are used, the former being of the thermo-electric or resistance type. Figs. 62 and 63 show the principle of a thermo-electric pyrometer of R. W. Paul, London.

The thermo-couple is made up of a platinum wire and a wire made from an alloy of platinum-iridium or platinum-rhodium. The wires are separated by a porcelain or quartz tube P, surrounded by an outer tube Q, closed at one end. This somewhat delicate structure is then packed in a sheath

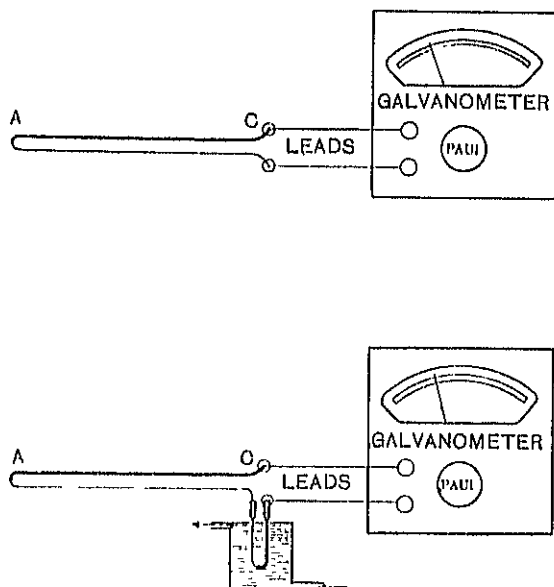


FIG. 62.--Principle of Electric Pyrometer.

of seamless steel tube S, asbestos twine A being loosely inserted between the tubes as shown. On subjecting the end of the pyrometer containing the junction of the two dissimilar metals to the heat of the oven, etc., and connecting the loose ends to a special galvanometer, a difference of potential is set up, causing a current to flow, varying in strength according to the temperature difference between the ends. In the type shown the cold ends are water-cooled to minimise errors due to casual heating of these ends. The galvanometer is calibrated to read in degrees Centigrade or

Fahrenheit as desired, the range of these instruments being from 0° to $1,100^{\circ}$, $1,300^{\circ}$, or $1,600^{\circ}$ C., according to the type chosen. The couple may be inserted in a coke oven flue, waste heat flue, boiler flue, or in the centre of a charge, and may be combined with apparatus giving a continuous record from which useful data as to the working of the plant may be secured. Radiation pyrometers are suitable for higher temperatures, and since this action depends on the radiation emitted by a hot body, the instrument may be placed at a

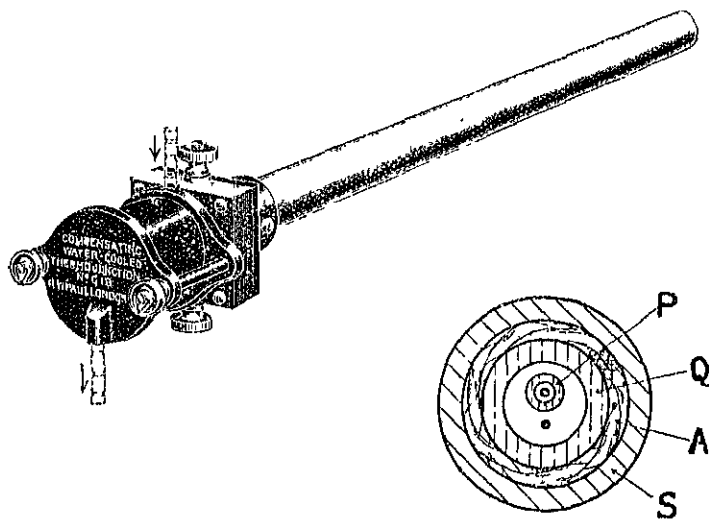


FIG. 63 -Electric Pyrometer. (R. W. Paul)

reasonable distance from the furnace, no portion of the instrument being actually in contact with the heated zone. In the Péry pyrometer (Cambridge Scientific Instrument Co.) the heat rays are received on a concave mirror, and focussed on to a sensitive thermo-couple connected to a millivoltmeter calibrated to read temperature directly. The radiation pyrometer of R. W. Paul dispenses with a focussing device, using a highly polished cone fitted at one end of a tube. The tube is pointed towards the hot body, and the heat rays are reflected on to a sensitive thermo-couple at the apex of the cone. The intensity of the heat rays is

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is inversely as the square of the distance, and the area of the hot body included in the field of vision, the amount is directly proportional to the distance. The two factors balance each other, and the result is thus independent of the distance. This method may be conveniently used for ascertaining the temperatures of boiler oven flues, or of the interior of furnaces when empty.

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inversely proportional to the square of the distance but since the area of the hot body included in the angle covered by the instrument is directly proportional to the same dimension, the two factors balance each other and the heat recorded is thus independent of the distance. Radiation pyrometers may be conveniently used for ascertaining the temperatures of coke oven flues, or of the interior of the ovens when empty.

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